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Reactions of Dimethylaniline with Some Resonance-stabilized Radicals

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Reactions of dimethylaniline with some resonance-stabilized radicals were studied. 2-Cyano-2-propyl radicals and 2-methoxycarbonyl-2-propyl radicals reacted to give *N*-methyl-*N*-(3,4-dicyano-3,4-dimethylpentyl)aniline and the corresponding 3,4-dimethoxycarbonyl derivative, respectively, while benzyl radicals and α-methoxycarbonylbenzyl radicals did not give reaction products with dimethylaniline. Mechanism of these reactions was proposed and it was pointed out that electron transfer from dimethylaniline to radicals was an important stage in these reactions.

Previously, one of the authors (N. I.) has studied the reaction of α,α'-azobisisobutyronitrile (AIBN) with some aromatic compounds and found that dimethylaniline reacts with 2-cyano-2-propyl radicals generated from AIBN.[1] We wish to report in this paper similar reactions of dimethylaniline with some resonance-stabilized radicals.

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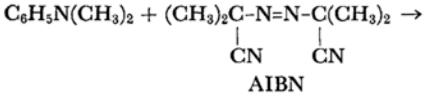
[1] N. Inamoto, *Yuki Gosei Kagaku Kyokaishi (J. Soc. Org. Synth. Chem. Japan)*, **17**, 174 (1959).

generated by the thermal decomposition of azo compounds or organomercurials.

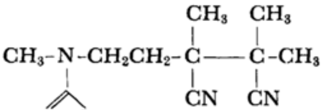
Results

Reaction with AIBN. The reaction of dimethylaniline with AIBN at water-bath temperature gave *N*-methyl-*N*-(3,4-dicyano-3,4-dimethylpentyl)-aniline (I)[2] in a 2.7% yield. The structure of I was determined by the NMR spectrum (Fig. 1) and the elemental analysis.

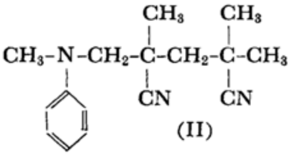


$$C_6H_5N(CH_3)_2 + (CH_3)_2\underset{CN}{C}-N{=}N-\underset{CN}{C}(CH_3)_2 \rightarrow$$

AIBN



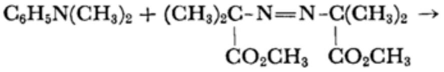
(I)



(II)

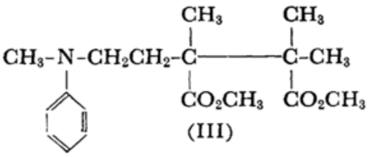
The NMR spectrum showed a singlet at τ 8.58 (9H, *C*-methyl protons), a multiplet between τ 7.8—8.5 (2H, methylene protons on C_β), a singlet at τ 7.13 (3H, *N*-methyl protons), a triplet at τ 6.55 (2H, J=7 cps, *N*-methylene protons), and a multiplet between τ 2.8—3.5 (5H, aromatic protons). That the structure of the product is not an isomeric one (II) was further confirmed by spin-spin decoupling technique. Thus, irradiation of the triplet at τ 6.55 caused the methylene multiplet between τ 7.8—8.5 to collapse to a typical AB type quartet. This fact shows that the methylene protons are on the carbon atom (C_β) adjacent to both the *N*-methylene group and the asymmetric center (C_γ).

Reaction with Dimethyl *α,α'*-Azobisisobutyrate (MAIB). The reaction of dimethylaniline with MAIB at *ca.* 100°C gave rise to *N*-methyl-*N*-(3,4-dimethoxycarbonyl-3,4-dimethylpentyl)aniline (III) in a 6% yield.



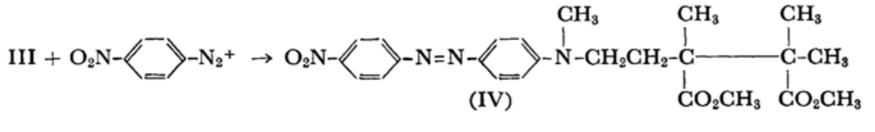
$$C_6H_5N(CH_3)_2 + (CH_3)_2\underset{CO_2CH_3}{C}-N{=}N-\underset{CO_2CH_3}{C}(CH_3)_2 \rightarrow$$

(MAIB)



(III)

The compound (III) was identified by elemental analyses and NMR spectra of both III and its azo derivative. The compound (III) is very viscous but distillable oil. It did not give crystalline derivatives; the picrate, hydrazide, quaternary ammonium salt and *N*-oxide were oily products, all of which could not be purified. *p*-Nitrobenzenediazonium salt, however, reacted with III to give a reddish brown crystalline product, which was identified to be an azo-coupling product (IV) by the elemental analysis and the NMR spectrum.



(IV)

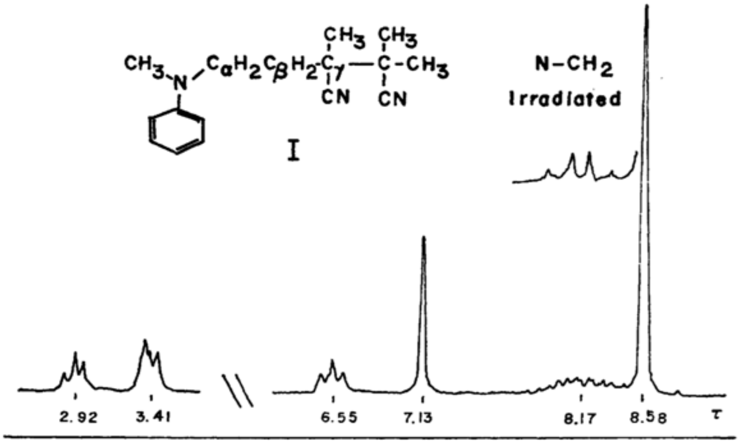


Fig. 1. NMR spectrum of the compound (I) in CCl_4 at 100 Mc.

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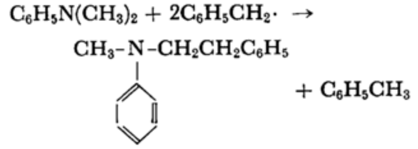
[2] The previously assumed structure[1] was found to be incorrect.

Reactions with Dibenzylmercury and Bis-(α-methoxycarbonylbenzyl)mercury. The reaction of dimethylaniline with dibenzylmercury, which is known to generate benzyl radicals by heating,[3] was carried out at 120—160°C under nitrogen. The reaction products obtained were only those derived from the thermal decomposition of dibenzylmercury; mercury (99%), bibenzyl (75%), and toluene (4%), no reaction products between dimethylaniline and benzyl radicals being obtained.

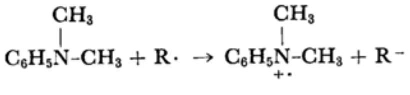
The reaction of dimethylaniline with bis(α-methoxycarbonylbenzyl)mercury (V)[4] was performed at 120—180°C under nitrogen. In this case, again, products were those attributed to the thermal decomposition of V; mercury (95%), *meso* form of dimethyl diphenylsuccinate (71%), and methyl phenylacetate (15%). However, in addition to these products a trace of bis(4-*N,N*-dimethylaminophenyl)methane was obtained.

Discussion

It has been shown in the present study that dimethylaniline reacts with 2-cyano-2-propyl radicals and 2-methoxycarbonyl-2-propyl radicals, but not with benzyl radicals, the latter were expected to form such a substitution product as follows.

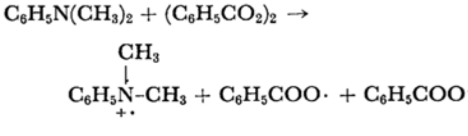


This fact suggests that in these reactions electron transfer as shown in Eq. (1) is an important process, because the reaction occurred only with radicals having electronegative groups which make the radicals R· more electrophilic and the corresponding carbanion more stable.



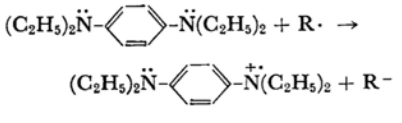
$$C_6H_5\overset{CH_3}{\overset{|}{N}}\text{-}CH_3 + R\cdot \rightarrow C_6H_5\underset{+\cdot}{\overset{CH_3}{\overset{|}{N}}}\text{-}CH_3 + R^- \quad (1)$$

It is known, indeed, that aromatic amines are readily subjected to one electron oxidation. Horner[5] and Imoto[6] have shown that the first stage in the reaction of dimethylaniline and benzoyl peroxide is electron transfer process from the former to the latter.



$$C_6H_5N(CH_3)_2 + (C_6H_5CO_2)_2 \rightarrow C_6H_5\underset{+\cdot}{\overset{CH_3}{\overset{|}{N}}}\text{-}CH_3 + C_6H_5COO\cdot + C_6H_5COO^- \quad (2)$$

Franzen[7] has reported that *N,N,N',N'*-tetramethyl-*p*-phenylenediamine is oxidized by various types of radicals, including 2-cyano-2-propyl radical, to give a stable cation radical, Wurster's salt.



(3)

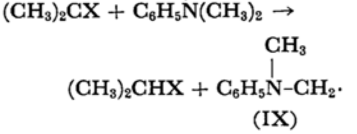
The conclusion that the more electrophilic the radicals R· are, the more readily the electron transfer occurs, has been drawn from the observation that, in radical polymerizations in the presence of dimethylaniline, the chain transfer for dimethylaniline becomes more effective when the end of a growing radical is more positive.[8]

On the basis of the facts described above, the mechanism of formation of I and III is considered as follows.

$$\underset{(VI)}{(CH_3)_2\dot{C}X} + C_6H_5\ddot{N}(CH_3)_2 \rightarrow$$

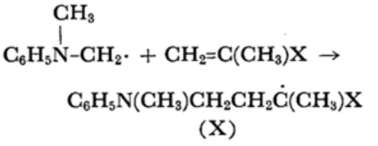
X=CN, COOCH₃

$$\underset{(VII)}{(CH_3)_2\overset{-}{C}X} + \underset{(VIII)}{C_6H_5\overset{+\cdot}{N}(CH_3)_2} \quad (4)$$

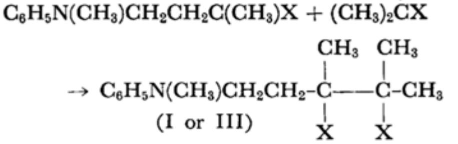


$$(CH_3)_2\overset{-}{C}X + C_6H_5\overset{+\cdot}{N}(CH_3)_2 \rightarrow (CH_3)_2CHX + \underset{(IX)}{C_6H_5\overset{CH_3}{\overset{|}{N}}\text{-}CH_2\cdot} \quad (5)$$

$$2(CH_3)_2\dot{C}X \rightarrow (CH_3)_2CHX + CH_2{=}C(CH_3)X \quad (6)$$



$$C_6H_5\overset{CH_3}{\overset{|}{N}}\text{-}CH_2\cdot + CH_2{=}C(CH_3)X \rightarrow \underset{(X)}{C_6H_5N(CH_3)CH_2CH_2\dot{C}(CH_3)X} \quad (7)$$



$$C_6H_5N(CH_3)CH_2CH_2\dot{C}(CH_3)X + (CH_3)_2\dot{C}X \rightarrow \underset{(I\ or\ III)}{C_6H_5N(CH_3)CH_2CH_2\text{-}\underset{X}{\overset{CH_3}{C}}\text{—}\underset{X}{\overset{CH_3}{C}}\text{-}CH_3} \quad (8)$$

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[3] A. G. Goble, A. G. Lidstone and P. J. S. Pauwels, *Chem. & Ind.*, **1959**, 1489.

[4] Reutov and his coworkers have reported the synthesis of this mercurial compound (V) and described its melting point was 140—141°C. However, although we synthesized V by the same method as that of Reutov and identified by the elemental analysis and the NMR spectrum, the melting point of V prepared by us was 181—183°C (dec.). The reason for this discrepancy was not clear but it seems to be attributed to stereochemical isomerism due to asymmetric carbons. See experimental part.

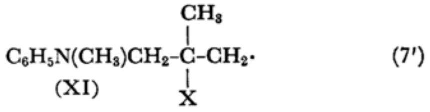
[5] L. Horner and E. Schenk, *Angew. Chem.*, **61**, 411 (1949).

[6] M. Imoto and S. Choe, *J. Polymer Sci.*, **15**, 485 (1955).

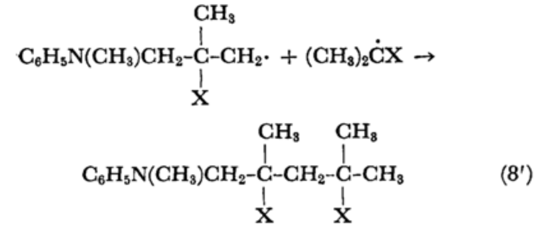
[7] V. Franzen, *Chem. Ber.*, **88**, 1697 (1955).

[8] M. Imoto, T. Otsu, T. Ota, H. Takatsugi and M. Matsuda, *J. Polymer Sci.*, **22**, 137 (1956).

$$C_6H_5N(CH_3)CH_2\cdot + (CH_3)XC{=}CH_2 \rightarrow$$



$$\underset{\text{(XI)}}{C_6H_5N(CH_3)CH_2}\text{-}\underset{X}{\overset{CH_3}{C}}\text{-}CH_2\cdot \qquad (7')$$



$$C_6H_5N(CH_3)CH_2\text{-}\underset{X}{\overset{CH_3}{C}}\text{-}CH_2\cdot + (CH_3)_2\dot{C}X \rightarrow$$

$$C_6H_5N(CH_3)CH_2\text{-}\underset{X}{\overset{CH_3}{C}}\text{-}CH_2\text{-}\underset{X}{\overset{CH_3}{C}}\text{-}CH_3 \qquad (8')$$

(II) X=CN

A cation radical (VIII) formed by electron transfer is deprotonated by a carbanion (VII) yielding a radical (IX). This radical (IX) adds to an olefin formed by disproportionation of a radical (VI) to give a radical (X), which successively couples with the radical (VI) to form the final product (I or III). Since the radical (X) is more stable than an isomeric one (XI) owing the conjugation with methyl and X groups, the addition reaction like Eq. (7′) and hence Eq. (8′) are not considered to occur.

Although direct hydrogen abstraction like Eq. (9) may be possible, it can be ruled out by the facts that (1) the radical (VI) is a poor hydrogen abstractor and (2) that, if the reaction proceeds by direct hydrogen abstraction, reactions like Eqs. (10) and (11) should occur in the reaction with benzyl radicals.

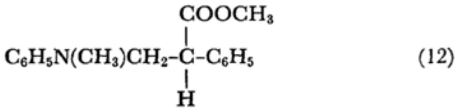
$$C_6H_5N(CH_3)_2 + (CH_3)_2\dot{C}X \rightarrow C_6H_5N(CH_3)CH_2\cdot + (CH_3)_2CHX \qquad (9)$$

$$C_6H_5N(CH_3)_2 + C_6H_5CH_2\cdot \rightarrow C_6H_5N(CH_3)CH_2\cdot + C_6H_5CH_3 \qquad (10)$$

$$C_6H_5N(CH_3)CH_2\cdot + C_6H_5CH_2\cdot \rightarrow C_6H_5N(CH_3)CH_2CH_2C_6H_5 \qquad (11)$$

The reason is not clear why the reaction between dimethyaniline and V (Eq. (12)) did not occur, because a radical (XII) generated from V is thought to be rather electrophilic like radicals VI.

$$C_6H_5N(CH_3)_2 + \underset{\text{(V)}}{[C_6H_5CH(COOCH_3)]_2Hg} \rightarrow$$



$$C_6H_5N(CH_3)CH_2\text{-}\underset{H}{\overset{COOCH_3}{C}}\text{-}C_6H_5 \qquad (12)$$

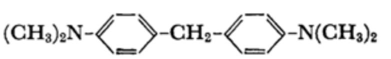
$C_6H_5\dot{C}HCOOCH_3$ (XII)

However, the formation of a trace amount of bis(4-*N*,*N*-dimethylaminophenyl)methane (XIII) may be considered to show that the reaction between dimethylaniline and the radical (XII) takes place at least to some extent, for the formation of the compound (XIII) can be explained reasonably by the reaction of dimethylaniline with formaldehyde (Eq. (13)) which is probably, though not conclusive, formed according to the following reactions.

$$C_6H_5\ddot{N}(CH_3)_2 + R\cdot \rightarrow C_6H_5\overset{+\cdot}{N}(CH_3)_2 + R^- \rightarrow \underset{\text{(IX)}}{C_6H_5N(CH_3)CH_2\cdot} + RH$$

$$IX + O_2 \rightarrow C_6H_5N(CH_3)CH_2OO\cdot \rightarrow C_6H_5N(CH_3)CH_2O\cdot \rightarrow C_6H_5\dot{N}CH_3 + CH_2O$$

$$2\,C_6H_5N(CH_3)_2 + CH_2O \rightarrow$$



(13)

(XIII)

The oxidation of the radical (IX) is considered to be due to a small amount of oxygen dissolved in the reaction solution.

Experimental

Materials. α,α'-Azobisisobutyronitrile (AIBN) was used after recrystallization of commercial product from ether, mp 103—104°C. Dimethyl α,α'-azobisisobutyrate (MAIB) was prepared from AIBN[9] and recrystallized from petroleum ether, mp 29—31°C. Dibenzylmercury was prepared by the method of Jones and Werner,[10] mp 110—111°C.

Bis(α-methoxycarbonylbenzyl)mercury(V) was prepared according to the directions of Reutov.[11] However, there was a great difference between the description by Reutov and our observation. Reutov and his coworkers have reported that the shaking of methyl α-bromophenylacetate with mercury for 2 hr gave 80% of methyl α-bromomercuriphenylacetate, mp 92.5—94.0°C, which reacted with ammonia in the chloroform solution to give rise to V in a 74% yield, mp 140—141°C. On the other hand, we found that the reaction of 40 g (0.18 mol) of methyl α-bromophenylacetate with 201 g (1 g atom) of mercury at room temperature for 3 hr gave 44 g of very viscous oil, which reacted with ammonia in the chloroform solution to form only 7.3 g (10%) of a crude mercurial compound. The crude product was recrystallized from ethanol. The purified one mostly but not perfectly melted at 155—157°C to become grey and turbid liquid, which melted perfectly at 181—183°C. NMR (in $CDCl_3$): τ 6.24 (6H), 6.03(2H), and 2.58(10H).

Found: C, 43.22; H, 3.67%. Calcd for $C_{18}H_{18}O_4Hg$: C, 43.33; H, 3.63%.

Different products were formed under a slightly vigorous condition. Thus, the reaction of 60 g (0.27 mol) of methyl α-bromophenylacetate with 270 g (1.35 g atom) of mercury at room temperature for 3 hr and then at 60°C for one hour resulted in the formation of 21 g (55%) of *meso* form of dimethyl diphenylsuccinate, mp 217—219°C (lit.,[12] 219—220°C),

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[9] J. Thiele and K. Heuser, *Ann.*, **290**, 35 (1896).

[10] L. W. Jones and L. Werner, *J. Am. Chem. Soc.*, **40**, 1266 (1918).

[11] O. A. Reutov, I. P. Beletskaya and G. A. Artamkina, *Zhur. Obshchei Khim.*, **30**, 3220 (1960).

[12] H. Wren and C. J. Still, *J. Chem. Soc.*, **111**, 1023 (1917).

3.5 g (9%) of racemic form of the same ester, mp 172—173°C (lit.,[13] 173—174°C) and a small amount of compound containing mercury, which was not identified.

Reaction with AIBN. a) The azonitrile (4.92 g, 0.030 mol) was added in small portions during one hour to dimethylaniline (18.15 g, 0.15 mol) heated on a steam bath, and the reaction solution was heated for additional few hours. The reaction solution was distilled under a current of steam in order to remove unchanged dimethylaniline and tetramethylsuccinodinitrile. The residue was extracted with ether, ether was evaporated, and 1 g of picric acid in alcohol was added. The precipitates thus obtained were recrystallized from ethanol to give 0.2 g (1.38%) of picrate, mp 150—151°C. When the reaction was carried out under the same condition as described above except further addition of 11.1 g of *n*-butanol to dimethylaniline, 0.35 g (2.4%) of the same picrate was obtained.

Found: C, 54.50; H, 5.24; N, 17.00%. Calcd for $C_{22}H_{24}N_6O_7$: C, 54.54; H, 4.99; N, 17.35%.

The picrate(0.3 g) was warmed with 20 *ml* of 28% aqueous ammonia to give a homogeneous solution. The reaction mixture was extracted with ether, the ethereal solution was dried with anhydrous potassium carbonate, ether was evaporated, and the residue was recrystallized from petroleum ether to give 100 mg (63.3%) of a compound, mp 72—73°C.

b) The same reaction was carried out using 90.8 g (0.75 mol) of dimethylaniline and 24.6 g (0.15 mol) of AIBN. After the reaction solution was distilled under atmospheric pressure to remove 2.1 g (10.1%) of isobutyronitrile, and then under reduced pressure to remove unchanged dimethylaniline and tetramethylsuccinodinitrile, the residue was extracted repeatedly with petroleum ether (bp 50—80°C). Condensation of the extract yielded crystals, which were recrystallized from petroleum ether to give 1.05 g (2.7%) of a compound of mp 72—73°C, which was the same as that obtained by the decomposition of the picrate in the procedure a).

Found: C, 75.25; H, 8.70; N, 16.39%. Calcd for $C_{16}H_{21}N_3$: C, 75.25; H, 8.29; N, 16.46%.

The IR spectrum of this compound (KBr disk) showed the presence of C≡N (2240 cm^{-1}) and N-CH_3 (2810 cm^{-1}). The NMR spectrum was shown in Fig. 1.

Reaction with MAIB. a) The reaction of 23 g (0.10 mol) of MAIB with 62 g (0.51 mol) of dimethylaniline was carried out by a similar procedure to that described in the reaction with AIBN. To the residue of steam distillation was added a saturated alcoholic solution of picric acid to give 0.29 g (1.9%) of crude picrate, which was brown viscous oil and could not be crystallized.

b) The azoester (69 g, 0.30 mol) was added in small portions to dimethylaniline (180 g, 1.50 mol) heated at 100—110°C and the reaction mixture was heated for 11 hr at this temperature. After methyl isobutyrate and dimethylaniline were distilled off, the residue was distilled under high vacuum in order to remove dimethyl tetramethylsuccinate, which distilled out up to 160°C (0.5 mmHg). The residue was 5.9 g of colorless and very viscous oil which distilled at 160—186°C (0.18 mmHg). The elemental analysis of the oil showed 3.8% of nitrogen content (calcd for $C_{18}H_{27}NO_4$: N, 4.36%), which indicated that it contained about 90% of the amine (III). The picrate of the crude amine was boiled with conc. aqueous ammonia to obtain free amine. Then it was twice purified by column chromatography on silica gel with benzene-ether (9 : 1) mixture as eluent.

Found: C, 67.21; H, 8.67; N, 4.51%. Calcd for $C_{18}H_{27}NO_4$: C, 67.26; H, 8.47; N, 4.36%.

The NMR spectrum of the purified amine in CCl_4 at 60 Mc: τ 8.90 and 8.85 (9H in total), 7.8—8.6 (multiplet, 2H), 7.17 (singlet, 3H), 6.76 (triplet, 2H, J=7 cps), 6.42 (singlet, 6H), and 2.7—3.7 (multiplet, 5H). Attempts to obtain crystalline derivatives were not successful except for a diazo-coupling product; the treatment of the crude amine with picric acid, hydrazine hydrate, methyl iodide, perbenzoic acid and conc. hydrochloric acid in order to obtain the corresponding picrate, hydrazide, ammonium salt, *N*-oxide, and free carboxylic acid, respectively, did not give crystalline products. The amine, however, underwent a diazo-coupling reaction with *p*-nitrobenzenediazonium chloride to yield reddish brown solid, which was recrystallized from carbon tetrachloride, mp 172—173°C. The NMR spectrum of the azo compound in $CDCl_3$ at 60 Mc: τ 8.76 (singlet, 9H), 7.5—8.5 (multiplet, 2H), 6.92 (singlet, 3H), 6.65 (triplet, 2H, J=7 cps), 6.25 (singlet, 3H), 6.33 (singlet, 3H), and 3.3—1.6 (multiplet, 8H).

Found: C, 60.85; H, 6.73; N, 12.18%. Calcd for $C_{24}H_{30}N_4O_6$: C, 61.16; H, 6.43; N, 11.91%.

Reaction with Dibenzylmercury. The solution of 15 g (0.04 mol) of dibenzylmercury in 24 g (0.2 mol) of dimethylaniline was heated under nitrogen at 120°C for one hour and at 160°C for half an hour. After mercury (7.94 g, 99%) was removed, the reaction mixture was distilled with steam. The distillate was extracted with ether and the ether solution was shaken with conc. hydrochloric acid. The aqueous layer was neutralized by aqueous solution of sodium carbonate, and extracted with ether. The ether solution was dried with anhydrous sodium sulfate and distilled to give only dimethylaniline. The ether layer was dried with anhydrous sodium sulfate, concentrated, and analyzed with glc using an apiezon grease column; 75% of bibenzyl and 4% of toluene were detected. The residue of the steam-distillation was extracted with ether, ether was evaporated, and then ethanol was added. Addition of picric acid to the ethanol solution gave only a trace amount of brown tarry compound, which was not identified.

Reaction with Bis(α-methoxycarbonylbenzyl)-mercury(V). The reaction between 13 g (0.11 mol) of dimethylaniline and 4.9 g (0.01 mol) of V was performed under nitrogen. Mercury began to deposit at about 120°C. The reaction temperature was gradually raised to 180°C during 30 min and kept at this temperature for 30 min. When the reaction solution was cooled, large quantities of white crystals precipitated. The precipitates were dissolved by adding of acetone and mercury isolated (1.87 g, 95%) was filtered off. To the acetone solution was added petroleum ether to give 2.1 g (71%) of white precipitates, which were identified by IR and mp (217—219°C) as *meso* form of dimethyl diphenylsuccinate. After distillation under reduced pressure in order to remove dimethylaniline, the filtrate was steam-distilled. The

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[13] H. Wren and C. J. Still, *ibid.*, **107**, 1453 (1915).

residue was extracted with methylene dichloride, the extract was dried, and methylene dichloride was evaporated to leave a small amount of purple oil. To the oil was added a saturated solution of picric acid in alcohol to form yellow precipitates. After ethanol was added enough to dissolve the yellow precipitates under reflux, the solution was cooled giving 0.29 g of crystals. Further recrystallization from ethanol gave yellow crystals of mp 180—181°C.

Found: C, 49.06; H, 3.69; N, 15.48%. Calcd for $C_{29}H_{28}N_8O_{14}$: C, 48.88; H, 3.69; N, 15.73%.

The picrate was decomposed by aqueous sodium hydroxide, the reaction solution was extracted with ether, and ether was evaporated leaving an almost white crystals. It was recrystallized from ethanol to give white crystals, mp 88—89°C. It was identified as bis(4-*N*,*N*-dimethylaminophenyl)methane (lit.,[14] mp 90°C). The NMR spectrum in CCl_4 at 60 Mc: τ 2.91 (12H), 3.71 (2H), 6.42, 6.63, 6.86, and 7.00 (8H, in total).

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[14] O. Doebner, *Ber.*, **12**, 810 (1879).