Amines as Dehalogenating Agents, III

The Fate of N,N-Dimethylaniline in the Reductive Dehalogenation of 3-Bromocamphor

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Debromination, 3-Bromocamphor, N,N-Dimethylaniline, Aniline

A product analysis was made for the reaction between some aromatic amines and 3-bromocamphor (2), which was invariably transformed into camphor (3) and eventually arylaminocamphor. The tertiary N,N-dimethylanilines were oxidized through a complex sequence of couplings and rearrangements to a number of diamines of the diphenylmethane type. Aniline (4) was also successful in the reductive debromination of 2 to 3 and camphor anil (7), but gave only tarry amino compounds. The reaction, carried out at 200 °C, appeared most probably to be triggered by the radicalic dissociation of the C–Br bond. Bromine ended up as bromide ion in a quantitative fashion.

We have used 3-bromocamphor (2) as the model compound, because its reaction with 1 is remarkably clean, giving camphor (3) in high yield. A standard base separation allowed to isolate a mixture of all basic nitrogen containing compounds. Bromide ion was found in practically quantitative conversions in the resulting water solution for longer reaction times (see Table I). At least eleven products could be separated by gas chromatography using suitable combinations of stationary phases and further identified by mass spectrometry (Table II), used both as a preliminary tool for structure determination and as a fingerprinting method for comparison with compounds obtained by different routes. The relative quantitative unimportance of products of such extremely high boiling points, that would not be eluted by gas chromatography was demonstrated by vacuum distillation (0.1 torr) of the amines mixture which left practically no residue (max. temp. 200 °C), although typical pH depending colors showed the presence of traces of high molecular weight dyes.

The more volatile components included aniline (4), N-methylaniline (5), p-bromo-N,N-dimethylaniline (6) and camphor anil (7). All the higher boiling components showed a dimeric framework, namely, that of variously N,N'-polymethylated o- and p-diaminodiphenylmethanes (DDM's). They are: N,N'-dimethyl-o,o'-DDM (8), N,N'-dimethyl-p,p'-DDM (9), N,N',N'-trimethyl-o,p'-DDM (10), N,N',N'-trimethyl-o,p'-DDM (11), N,N',N'-trimethyl-p,p'-DDM (12), N,N',N',N'-tetramethyl-o,p'-DDM (13) and N,N',N',N'-tetramethyl-p,p'-DDM (14). The mass spectrum of the GC peak with retention time ratio 0.57 with respect to 11 in the analysis with SE 30 as stationary phase and the mass spectrum of the GC peak with retention time ratio 1.00 in the analysis with Versamide, respectively belonging mainly to 11 and 14, showed the presence of the molecular ion of another N,N'-poly-methylated-DDM, i.e., N,N'-dimethyl-o,p'-DDM (15). This compound was prepared by an independent route and found to have the same GC properties; it showed the same mass spectrum as the one reconstructed for the hidden peak. Camphor anil

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### Table I. Products of the reaction between 3-bromocamphor (2) and aromatic amines.

<table>
<thead>
<tr>
<th>Amine</th>
<th>Time [h]</th>
<th>Br- Camphor</th>
<th>Products [%]</th>
<th>Nitrogen containing compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,N-Dimethylaniline (1)</td>
<td>3</td>
<td>29</td>
<td>33</td>
<td>b</td>
</tr>
<tr>
<td>N,N-Dimethylaniline (1)</td>
<td>8</td>
<td>47</td>
<td>50</td>
<td>Aniline (4, 1) N,N-Dimethylaniline (5, 87) p-Bromo-N,N-dimethylaniline (6, 0.5) Camphor anil (7, 1) N,N'-Dimethyl-o,o'-DDM (8, 1) N,N'-Dimethyl-p,p'-DDM (9, 2) N,N,N'-Trimethyl-o,p'-DDM (10, 1) N,N,N'-Trimethyl-o,p'-DDM (11, 9) N,N,N'-Trimethyl-p,p'-DDM (12, 7) N,N,N',N'-Tetramethyl-o,p'-DDM (13, 3) N,N,N',N'-Tetramethyl-o,p'-DDM (14, 29) N,N'-Dimethyl-o,p'-DDM (15)c</td>
</tr>
<tr>
<td>N,N-Dimethylaniline (1) and 18</td>
<td>3</td>
<td>c</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>Aniline (4)</td>
<td>24</td>
<td>98</td>
<td>7</td>
<td>Camphor anil (7, 87) N,N-Diphenylamine (25, 9)</td>
</tr>
<tr>
<td>p-Toluidine (22)</td>
<td>24</td>
<td>c</td>
<td>26</td>
<td>Aniline (4, 3)d Camphor anil (7, 1) N,N-Di-p-tolylamine (42, 3)</td>
</tr>
<tr>
<td>N,N-Dimethyl-p-toluidine (34)</td>
<td>8</td>
<td>58</td>
<td>2,2'-Di(N-methyl-4-toluidino)methane (35, 17) N,N,N'-Trimethyl-2,2'-di(4-toluidino)methane (36, 20) 2,2'-Di(N,N-dimethyl-4-toluidino)methane (37, 5)</td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>3</td>
<td>c</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>8</td>
<td>1.5</td>
<td>7</td>
<td></td>
</tr>
</tbody>
</table>

a Temperature of the thermostatic external bath: 200 °C ± 3 °C. The amine/2 weight ratio was 5:1.
b Yields not determined, same qualitative product pattern as in analogous experiments.
c Yield not determined.
d Yield based on initial amine.

### Table II. GC-MS data of DDM's (8-15) from reactiona of 3-bromocamphor (2) and N,N-dimethylaniline (1).

<table>
<thead>
<tr>
<th>DDM</th>
<th>GC Retention ratiosb</th>
<th>Mass spectrometry at 70 eV, m/e (% rel. int.)c</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,N'-Dimethyl-o,o'-DDM (8)</td>
<td>0.61</td>
<td>0.35</td>
</tr>
<tr>
<td>N,N'-Dimethyl-o,p'-DDM (9)</td>
<td>1.98</td>
<td>0.88</td>
</tr>
<tr>
<td>N,N,N'-Trimethyl-o,p'-DDM (10)</td>
<td>0.37</td>
<td>0.30</td>
</tr>
<tr>
<td>N,N,N'-Trimethyl-o,p'-DDM (11)</td>
<td>0.70</td>
<td>0.57</td>
</tr>
<tr>
<td>N,N,N'-Trimethyl-p,p'-DDM (12)</td>
<td>1.41</td>
<td>0.92</td>
</tr>
<tr>
<td>N,N,N',N'-Tetramethyl-o,p'-DDM (13)</td>
<td>0.44</td>
<td>0.46</td>
</tr>
<tr>
<td>N,N,N',N'-Tetramethyl-o,p'-DDM (14)</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>N,N'-Dimethyl-o,p'-DDM (15)</td>
<td>1.00</td>
<td>0.57</td>
</tr>
</tbody>
</table>

a Actual experiment described in the experimental section.
b Columns: 2 m by 0.25 mm, copper, Versamide 3% on Chromosorb W (80–100 mesh) and SE 30 1% on Chromosorb P (80–100 mesh), respectively at 200 °C and at 180 °C; flow rate 30 ml/min (N2), injector at 300 °C, manifold at 300 °C. Compound 14 was taken as internal standard.
c Spectra were recorded via the GC inlet, unless specified otherwise.
d MS recorded via direct inlet.
(7), 9 and 14 were prepared according to known methods. Partial methylation of 9 with methyl iodide gave 12. o-(N-Methylamino)benzyl alcohol (16) was condensed with N,N-dimethylaniline (1) and N,N-dimethylanilinium bromide (17) to give mainly 11 and some 13: the ratio of these two products was found to depend on the reaction temperature. Compound 13 appeared to be produced via N-methylation by 17. The same alcohol 16 with N-methylaniline (5) and N-methylanilinium bromide (18) gave as the major product 15 with minor amounts of 8. No N-methylation took place in this instance. A priori, compound 10, present in small amount in the mixture of the reaction of 1 with 2, and for which no independent synthesis was made, with its molecular weight 240 could have either the proposed structure of the isomeric one of N,N,N',N'-tetramethyl-o,o'-DDM (19). We think that 19 is not in the mixture on two grounds: the corresponding N,N,N',N'-tetramethyl-o,o'-DDM is not present, most probably because of steric reasons, and in force of an extrapolation of the rationale explaining the relative variation of the m/e 134 and 120 peak intensity in the mass spectrum, as could be learnt from the mass spectra of 11 and 12 (quem vide, Table II): in fact release of steric compression facilitated the formation of the ion at m/e 120 for 10.

Discussion

The product analysis of the reaction between 1 and 2 appeared to be rather satisfactory: e.g., in an experiment with 50% yield of camphor (3), we obtained bromide ion and oxidized N,N-dimethylaniline products of the DDM type respectively in 47% and 52% yield. Bromide ion was determined potentiometrically in water solution, whereas the yields of the organic material were determined by GC using internal standards.

Although we are unable to draw any definitive mechanistic conclusions at the present time, we feel that some discussion about the a priori possible pathways to the observed products is pertinent. We shall review them critically, pointing to the relative merits and disagreements with observations now available to us.

3-Bromocamphor (2) is known to show none of the high electrophilic reactivity (S_{2}2 reaction) of common α-bromoketones, most probably because of steric hindrance to either exo or endo approach of a base to the 3-carbon atom; 2 would not react with "any" amines, say, up to 100 °C to yield quaternized ammonium ions. If this reaction were possible at higher temperatures with relatively bulky and not so basic amines like 1, the reaction product 20 could further go on to the reduced ketone through an ever appealing six member transition state (Scheme I). In this case, the collapse of 20 to products, should be faster than the quaternization reaction.

An S_{N}1 reaction could also lead to 20, but this must be considered a forbidden proposal in con-
connection with an α-bromoketone, moreover under not exactly solvolytic conditions. We feel that the mechanism envisaging 20 as a precursor to 3 is anyhow not correct, in view of the fact that both aniline (4) and p-toluidine (22), for which no such reaction can apply reacted with 2 at rates comparable with 1 to yield 3 or the product of subsequent reaction of 3 with these amines: 7 and camphor p-methylanil (23) respectively (Table I). If nitrogen quaternization had occurred to any large extent as necessary to support the above mechanism, the less bulky amines 4 and 22 should have reacted more easily than 1, thus subtracting 2 and 3 from material balance and largely suppressing the reduction reaction. The expected product from this reaction should be 3-anilinocamphor (24), when aniline (4) was the reactant (Scheme II). Any such product was absent as in the N,N-dimethylaniline reaction, where it might have originated by a certainly easy\(^7\) N-demethylation of 20.

Another mechanistic possibility is an S\(_{N}\)2 reaction at the partially positive\(^8\) bromine atom, leading to abstraction of the halogen, formation of the camphor enolate (25) and N-bromo-N,N-dimethyl-anilinium ion (26). These intermediates would eventually generate 3 by protonation and most probably 6 by rearrangement. As an alternative to the latter pathway, 21 could be formed \(\text{via}\) hydrogen bromide 1,2-elimination, a much less favoured bimolecular reaction (Scheme III). \(p\)-Bromo-N,N-dimethylaniline (6), in fact, could form even in a direct nucleophilic attack by the \(para\) position of 1 at the bromine atom of 2. But 6 was just a minor reaction product, when 1 was used. \(C\)-Brominated amines were absent both in the aniline (4) and in the \(p\)-toluidine (22) experiments. \(N\)-Brominated intermediates of the latter amines 4 and 22 should rearrange to undetected \(C\)-Brominated products, like \(p\)-bromoaniline (27). As we saw, practically all bromine was converted to bromide ion in all the reductions of 2 with amines. The two primary amines 4 and 22 were then oxidized to different products which appeared as dark polymers. Incidentally, in the experiment with 4, collateral reactions gave \(N,N\)-diphenylamine (25)\(^9\) and camphor anil (7), for which the reaction conditions are just right to produce then from 3 and 4. If we consider that “positive” bromine compounds, like N-bromoamides are known to give ring brominated products in high yields in the reaction with aromatic amines\(^10\), we can therefore conclude that, if an incursion of the bromonium ion abstraction mechanism cannot be ruled out, it must be of very minor importance to the overall process.

A one electron transfer from 1 to 2 could be the triggering step of the process, 3-bromocamphor anion radical (29) and \(N,N\)-dimethyl-N-phenyl-anilinium ion (30) being its reaction products, possibly associated as an ion pair. Ion 30 would subsequently give up a hydrogen atom to the radical 31, formed by a bromide ion expulsion from 29 (Scheme IV). The observation that an initial high acidity of the medium, expected to speed up the reaction by protonating 2, had on the contrary a disactivating effect (Table I) makes this pathway doubtful. It should be added that a very preliminary study of the electrochemical behaviour of 1 and 2 at room temperature in acetonitrile by potential sweep voltammetry has shown that both the reduction of 1 and the oxidation of 2 are irreversible. The peak potentials determined by cyclic voltametry are respectively \(E_{\text{ox}} + 0.88\) volt for 1 and \(E_{\text{red}} - 1.42\)
volt for 2. Due to the irreversibility of the processes up to the highest velocities employed (100 volt sec⁻¹), these values cannot be used to evaluate directly the Gibbs function change for the electron transfer reaction. However, the presence of two peaks in the oxidation curve of 2, attributed to the oxidation of the bromide ion, must be due to a successive chemical process, from which it can be inferred that the actual potential might be even more negative. Moreover, in the case of the oxidation of 1, the irreversibility seems to be due to a coupling reaction of the initially produced radical cation 30⁺. In conclusion, under these conditions, the large difference between the electrochemical potentials for the two reactions would signify that the electron transfer is thermodynamically forbidden.

A separate experiment of thermolysis of 2 without added amine gave some camphor (3). Although a complete analysis of this reaction is not available at this stage, this is a definite indication that a radical cleavage of the carbon-bromine bond as the initial step is strongly suggested. The radical products of this first step would then react on as outlined in Scheme V. Formation of radical 32 was already observed in the thermal decomposition of di-t-butylperoxide in 1 and the fate of 1 was found to depend on the presence of proton donors. When acids were added to the mixtures disproportionation of 32 took place with final formation of 14, isolated by absorption chromatography. It is remarkable that the very reactive bromine atom apparently enters a selective hydrogen abstraction reaction with little aromatic radical substitution (product 6) and perhaps no oxidative action (to 30)¹³. To our knowledge, this is the first reported instance of the reaction of a bromine atom with an aniline.

Every mechanism we have discussed lead to the ion 21, which is the necessary intermediate to the observed products of oxidation of 1. Scheme VI summarizes the essential steps to all the N,N'-polymethylated DDM identified from this reaction. It is to be stressed that such an intermediate has never been isolated. We may expect a high electrophilic aromatic reactivity from 21 in presence of strongly nucleophilic material like aromatic amines. N-
Dealkylation and realkylation of aromatic amines are commonplace at such a temperature, as in the Hofmann-Martius rearrangements; whence we find both monomeric aniline (4) and N-methylaniline (5) and dimeric compounds with different degrees of N-methylation. The exclusive ortho and para substitution pattern of the dimeric products was a clear indication of the ionic pathway of the cou-
pling reactions\(^{15}\). Not necessarily all compounds need to form from a direct C-alkylation. Nuclear C to C migrations are greatly favoured by two factors: the great proton affinity of the ortho and para positions and the great stabilization of the eventually leaving ring-aminosubstituted benzyl substituents. We have collected some evidence about the mobility of such substituents\(^{16}\).

The alternative mechanism (Scheme VII) for the formation of the DDM’s 8–15 is that of a direct reaction of the amines 1 and 5 with formaldehyde (33), reaction (3), formed by a possible hydrolysis (reaction (2)) of 21 by water produced by anil formation (reaction (1)). In fact, only catalytic amounts of water would be needed and such reactions were just those employed in this work to prepare 9 and 14 according to known procedures\(^4\). In absence of reactivity data on 21, if this mechanism were the correct one, reaction of 21 with little water should be much faster than direct coupling with 1 and 5. Also trapping of formaldehyde (33) by 1 and 5 should be extremely efficient and competitive with self polymerization, favoured by the fundamentally basic substrate and partly hampered by the high temperature, because the yields of DDM’s 8–15 were high. Experiment bound for trapping formaldehyde (33) failed to reveal any.

An indirect evidence against this mechanism

![Schema VII](image)

**Table III. MS data of DDM's (35–37) from reaction\(^a\) of 3-bromocamphor (2) and N,N-dimethyl-p-toluidine (34).**

<table>
<thead>
<tr>
<th>DDM</th>
<th>Mass spectrometry at 70 eV, m/e (% rel. int.)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2'-Di(N-methyl-4-toluidino)methane (35)</td>
<td>121 (100), 254 (M(^+), 96), 134 (89), 132 (45), 120 (40), 222 (20), 105 (19), 255 (19), 122 (18), 133 (17).</td>
</tr>
<tr>
<td>N,N,N'-Trimethyl-2,2'-di(4-toluidino)methane (36)</td>
<td>268 (M(^+), 100), 134 (71), 135 (69), 132 (57), 146 (41), 147 (30), 222 (22), 269 (21), 105 (20), 117 (20).</td>
</tr>
<tr>
<td>2,2'-Di(N,N-dimethyl-4-toluidino)methane (37)</td>
<td>134 (100), 148 (54), 132 (49), 282 (M(^+), 47), 44 (26), 135 (26), 146 (24), 133 (19), 105 (19), 59 (18).</td>
</tr>
</tbody>
</table>

\(^a\) Actual experiment described in the experimental section.

\(^b\) Spectra were recorded via the GC inlet.
came from the reaction of 2 with N,N-dimethyl-p-toluidine (34). Camphor (3) was obtained; the oxidized products from 34 were \( p,p' \)-dimethyl-o,o'-DDM's 35, 36, 37 and an unidentified snow white polymer soluble in neutral or acidic water, but insoluble in basic solution (Scheme VIII). When formaldehyde (33) was treated with 34 in acidic medium no polymer formed and a very different product pattern resulted.

**Experimental**

**Materials and equipment**

Mono-free N,N-dimethylaniline (1), aniline (4), and N-methylaniline (5) were purified by distillation under reduced pressure before use. 3-Bromocamphor (2), camphor (3), p-toluidine (22), N,N-dimethyl-p-toluidine (34) and methyl N-methylantranlylate (38) were checked by GC and used as received. Camphor anil (7), N,N'-dimethyl-p,p'-DDM (9), N,N,N',N'-tetramethyl-p,p'-DDM (14), camphor p-methylanilin (23), 3,3-dibromocamphor (39), N,N,N',N'-tetramethylanilinbenzidine (40) and N,N'-dimethyl-N,N'-diphenylethelenediamine (41) were prepared according to described methods. The hydrobromides 17 and 18 of 1 and 5 were prepared by vacuum evaporation of water from a solution of the corresponding amines in an equivalent amount of 45% hydrobromic acid.

Infrared spectra were recorded with a Perkin Elmer Infrared Spectrophotometer 710 B; band calibration was made by the use of a polystyrene film. Spectra were recorded on neat liquids or with the KBr pellet method for solids. Proton NMR spectra were recorded with a Perkin Elmer NMR spectrometer R 12 B; peak locations are given in \( \delta \) values (ppm) using TMS as internal standard.

Gas chromatograms were obtained with a Perkin Elmer 900 Gas Chromatograph using nitrogen as carrier gas and a flame ionization detector. Steel and copper (0.25 cm i. d. by 2 m length) columns as well as glass (0.30 cm i. d. by 2 m length) columns, with a variety of stationary phases (SF 96 2-4%, SE 30 1%, Versamide 3-5% and FFAP 4% on Chromosorb W 80-100 mesh) were used with suitable programming between 80-300 °C. Mass spectra were recorded with an LKB 9000 Gaschromatograph-Mass Spectrometer (electron impact) both using the direct inlet system and the GC inlet at 70 eV electron energy. The recorded spectra have both ion source and GC backgrounds subtracted.

\[ N,N'-Dimethylaniline (1) \text{ and } 3\text{-bromocamphor (2)} \]

A typical experiment was as follows. The amine (1, 5 g) and 2 (1 g) were heated during eight hours on an oil bath at 200 °C (refux). Some white amine salt sublimed into the neck of the flask. The dark reaction mixture was quickly extracted with ether and concentrated cold aqueous ammonia. The aqueous solution was assayed for bromide ion determination (yield: 47%), performed potentiometrically. The ether extract was treated with cold (-15 °C) concentrated hydrochloric acid. The aqueous layer was immediately made strongly alkaline with cold concentrated sodium hydroxide, extracted with ether and dried over sodium sulfate (amine ether solution: AES). GC preliminary analysis of the AES showed the presence of 12 components. GC-ms analysis revealed their identity: aniline (4, 1%)\(^{21}\), N-methylaniline (5, 87%), N,N-dimethylaniline (1), p-bromo-N,N-dimethylaniline (6, 0.5%), camphor anil (7, 1%) and eight different N,N'-polymethylated DDM's. Yields and GC-ms properties of the DDM compounds are shown in Tables I and II. Vacuum distillation of the amine mixture with a simple apparatus gave a lower boiling fraction containing 1, 4 and 5, but did not separate any of the other components to a reasonable degree of purity. It was possible to
obtain 14 in a crystalline state by repeated crystallizations of the last fraction, b.p. 148–162 °C (0.1 torr), mp. 88–90 °C (mmp.: no depression). The identification of all other amines was based on the comparison of their GC retention (enhancing technique and retention times ratios) and ms properties with those of compounds obtained by different routes, whenever these were prepared.

In a 3 h experiment under the same conditions 9.5 mmol of 1 were present as hydrobromide from the beginning of the reaction. The results are shown in Table 1.

<table>
<thead>
<tr>
<th>N,N,N'-Trimethyl-p,p'-diaminodiphenylmethane (12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>To 9 (4.4 mmol) dissolved in methanol (8 ml), iodomethane (4.4 mmol) was added at room temperature. The mixture was kept at 50 °C in a closed flask during 90 min. Solvent and unreacted iodomethane were evaporated and the amines were extracted with aqueous sodium hydroxide and ether. GC-ms analysis of the ether extract showed the presence of the three amines 9, 12 and 14 in the ratio 1:2:2.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>N,N'-Dimethyl-o,p'-diaminodiphenylmethane (15) and N,N'-Dimethyl-o,p'-diaminodiphenylmethane (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl N-methylantranilate (38, 37 mmol) in anhydrous ethyl ether (100 ml) was treated with lithium aluminum hydride (55 m f) added portionwise without temperature control. After standing at room temperature during 16 h, the mixture was refluxed during 2 h and finally quenched with ethyl acetate followed by water. o-(N-Methyl)-aminobenzylalcohol (16), b.p. 90 °C (0.1 torr) was obtained in good yield. Its properties were in agreement with those reported in the literature. A mixture of this alcohol (4.2 mmol), N-methylaniline (5, 14.5 mmol) and N-methylanilinium bromide (18, 10 mmol) were kept at 100 °C during 7 h. The ether extract after treatment with cold sodium hydroxide showed the presence of the wanted products 8 and 15 in the ratio 1:11 as showed by GC–ms analysis. The overall yield was 101% (GC). Microsublimation gave a slightly yellow oil of the same composition.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>N,N',N'-Trimethyl-o,p'-diaminodiphenylmethane (11) and N,N',N'-Trimethyl-o,p'-diaminodiphenylmethane (13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>The alcohol 16 (3.5 mmol), N,N-dimethylaniline (1, 12 mmol) and N,N-dimethylanilinium bromide (17, 10 mmf) were kept at 80 °C during 150 min. Work up gave an ether solution containing 11 (yield: 73%). The solvent was evaporated, N,N-dimethylaniline (1) was distilled under reduced pressure and 11 was purifed by sublimation, m.p. 82–84 °C, IR (on the liquid undercooled): 3440 m, 3140 vw, 3080 w, 3055 m, 3030 m, 2990 m, 2940 s, 2900 s, 2825 s, 2635 vw, 2580 vw, 1890 vw, 1675 vw, 1615 s, 1590 s, 1565 m, 1520 s, 1485 s, 1470 s, 1455 s, 1355 s, 1320 s, 1280 m, 1270 s, 1235 s, 1200 m, 1170 s, 1135 m, 1105 w, 1070 m, 1050 m, 955 s, 915 w, 860 w, 835 m, 810 s, 755 s, 720 w and 695 w cm⁻¹. NMR (CDCl3): 2.76 (s, 3H), 2.90 (s, 6H), 3.80 (s, 2H) and 6.94 (m, 8H). In another experiment the same amounts of the reagents were kept at 110 °C during 4 h. Ether extraction of the reaction mixture, after treatment with aqueous cold sodium hydroxide gave a solution containing four major components as shown by GC–ms: the two wanted products 11 and 13 (yields: 35% and 26% respectively) and, in addition, 14 (14%) and 12 (6%).</td>
</tr>
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</table>

### 3-Bromocamphor (2) and aniline (4)

Aniline (4, 5 g) and 3-bromocamphor (2, 1 g) were heated during 24 h at 200 °C on an oil bath. The cooled solution was treated with aqueous 30% sodium hydroxide (15 ml) and extracted with ether. Tar formation was extensive. The dark ether solution was then worked up as described for the N,N-dimethylaniline reaction, obtaining a dark AES and a colorless NES. The former contained camphor anil (7, 87%) and N,N-diphenylamine (28, 9%, calculated on initial aniline). The latter contained compor (3, 7%) and unreacted 2 (2%). No other product was detected by GC. The yield of bromide ion was 98%.

### 3-Bromocamphor (2) and p-toluidine (22)

The reaction was run as described for aniline. Camphor (3) was formed in 26% yield. All 3-bromocamphor (2) had disappeared. Camphor p-methyl-anilin (23) was obtained in 51% yield. The AES contained also N,N-di(p-tolyl)amine (42) together with a number of products of C-demethylation, i.e., aniline (4), camphor anil (7) and N-phenyl-p-toluindine (43). In the amine mixture GC–ms analysis at high temperature (240 °C) on a silicone column revealed the presence of a compound with a molecular weight 312 (M⁺), exhibiting ms fragmentations with losses of either a methyl group or C₇H₇ from the parent ion. This compound, whose structure was not elucidated, disappeared after a few hours' standing in the AES at low temperature.

### 3-Bromocamphor (2) and N,N-Dimethyl-p-toluindine (34)

The reaction was carried out after exactly the same fashion as for 1. Treatment of the cooled mixture with 30% aqueous sodium hydroxide and ether caused the formation of a large amount of a partly water (pH 7) soluble white polymer, which was separated. The ether solution underwent the usual acid base separation. The NES contained camphor (3, 68%) and unreacted 2 (41%). The higher temperature GC–ms analysis showed the presence of three components, which, on the basis of their mass spectra, were identified as the following compounds: 2,2'-di(N,N-dimethyl-4-toluindino)methane (37, 5%), N,N,N'-trimethyl-2,2'-di(4-
Toluidino)methane (36, 20%) and 2,2'-di(N-methyl-4-toluidino)methane (35, 17%).

**Thermolysis of 3-bromocamphor (2)**

A) The ketone 2 was kept at 200 °C in a sealed evacuated glass tube during 3 h. Upon opening the tube, little HBr evolved. The solid and dark mixture was taken up with ether; some powdery black material did not dissolve. GC–ms analysis showed only two components, unreacted 2 and 3, in the mole ratio 7.5:1. 3,3-Dibromocamphor (39) was absent. The recovery of 2 and 3 amounted to 59%.

B) The ketone 2 was heated during 8 h at 200 °C in a round bottom flask equipped with a Claisen condenser, a receiver kept at —20 °C and an HBr trap (15 ml water). Rather extensive tar production was observed, but only 1.5% HBr was obtained. Camphor (3) and 2 were the only components of the reaction mixture revealed by GC over a wide range of temperatures (50–300 °C).

**N,N-Dimethylaniline (1) and N,N-dimethylanilinium bromide (17)**

The amine 1 (42 mmol) and 17 (2.5 mmol) were kept at 200 °C during 8 h. After treatment with 30% chilled aqueous sodium hydroxide and ether, the organic phase was found to contain N-methyl-aniline (5, 4.8%) beside unreacted starting material. In an experiment with less 17 (1.2 mmol), 5 was produced in 1.5% yield.

**N,N-Dimethyl-p-toluidine (34) and formaldehyde (33)**

The amine (34, 55 mmol), aqueous 40% formaldehyde (33, 45 mmol) and concentrated hydrochloric acid (2 ml) were admixed in this order and the mixture stirred at 100 °C during 5 h in a well ventilated hood. Sodium hydroxide was added and the mixture was extracted with ether. GC–ms analysis showed the presence of 37, which was the major component, together with two unidentified diamines (M+ 282 and 296, respectively).

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5. W. Micheler and G. Moro, Chem. Ber. 12, 1167 [1879].
9. The reaction with p-toluidine (22) gave the corresponding amine N,N-di(p-tolyl)amine (42) and N-phenyl-p-toluidine (43), arising from C-demethylation of the former and of 22. Camphor anil (7) also formed in this reaction according to analogous processes.
13. In case an oxidative action to 30 took place, the radical cation would have to undergo disproportionation to 21 and 33. 30 could be expected to react with 1 to eventually yield N,N,N',N'-tetramethyl-p,p'-benzidine (40, D. M. Graham and R. B. Messrobin, Can. J. Chem. 41, 2945 [1963]), a compound definitely not present in the reaction mixture.
14. We found an unexplained net 30% excess of this product over the maximum amount expected for the disproportionation of 1 and the expulsion of 5 from reaction intermediates (see Scheme VI).
17. P. Lipp and G. Stutzinger, Chem. Ber. 65, 241 [1932]; m.p. 31–34 °C, IR (liquid): 3040 w, 2965 s, 2940 s, 2880 m, 2830 w, 1685 s, 1660 w, 1620 w, 1565 m, 1490 w, 1455 m, 1430 w, 1395 s, 1375 w, 1225 m, 1105 w, 1065 w, 840 m, 765 w and 745 w cm⁻¹, NMR (CCl₄): 0.85 (s, 3H), 0.98 (s, 3H), 1.65 (s, 3H), 2.29 (s, 3H) and 6.78 (q, 4H); MS: 241 (M⁺ 100), 133 (64), 95 (60), 91 (40), 107 (46), 59 (38), 107 (38), 41 (34) and 45 (31).
20. J. G. M. Dunlop and H. O. Jones, J. Chem. Soc. 1909, 416; IR (KBr): 3500 s, 1590 s, 1495 s, 1475 s, 1440 m, 1365 s, 1320 m, 1235 m, 1190 s, 1095 m, 1035 w, 990 m, 950 w, 855 w, 740 s and 660 cm⁻¹, NMR (CCl₄): 2.75 (s, 6H), 3.52 (s, 4H), 6.60 (s, 4H).
6.31 (m, 6H) and 6.78 (m, 4H), MS: 120 (100), 77 (21), 121 (17), 240 (M+ 13), 104 (11), 105 (11), 91 (7), 51 (7), 42 (7) and 79 (4).

Calculated on initial 2.
