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Molecular Rearrangements. VII. *N*-Alkylarylamines (III). Thermal Rearrangement of Secondary Arylamines

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Heating of *N*-benzyl-*o*- and *p*-toluidines resulted in migration of the benzyl group to the corresponding toluidine nucleus. The pyrolysis of *N*-benzyl-*o*-toluidine produced ammonia, toluene, bibenzyl, *trans*-stilbene, *o*-toluidine together with 4-amino-3-methyldiphenylmethane and 2,3-diphenyl-7-methylindole. *N*-benzyl-*p*-toluidine resulted into the same neutral products together with ammonia, *p*-toluidine, 2,3-diphenyl-5-methylindole together with 2,7-dimethyl-9-phenylacridine. Using phenol or quinoline as solvents, the normal rearranged products were accompanied with 2- and 4-benzylphenols and 2- and 4-benzylquinolines. It was concluded that the pyrolysis of the secondary amines proceeds through their homolytic fission to benzyl and the corresponding toluidino free radicals. Homolysis of some primary products was also observed.

The present paper describes a thermal rearrangement of *N*-benzyl-*o*- and -*p*-toluidines, involding a homolytic fission of the alkyl–*N*-bond. *N*-Benzyl-*o*-toluidine changed on heating in nitrogen atmosphere at about 333 °C to give ammonia, toluene, bibenzyl, *trans*-stilbene, *o*-toluidine, 4-amino-3-methyldiphenylmethane, and 2,3-diphenyl-7-methylindole.

Similarly, *N*-benzyl-*p*-toluidine, under similar conditions at 315 °C, underwent pyrolysis to afford the same neutral products, ammonia, *p*-toluidine, 2,3-diphenyl-5-methylindole and 2,7-dimethyl-9-phenylacridine.

Heating each of *N*-benzyl-*o*- and -*p*-toluidine at its boiling point for several days, gave about the same products but in lower yields, together with some benzaldehyde.

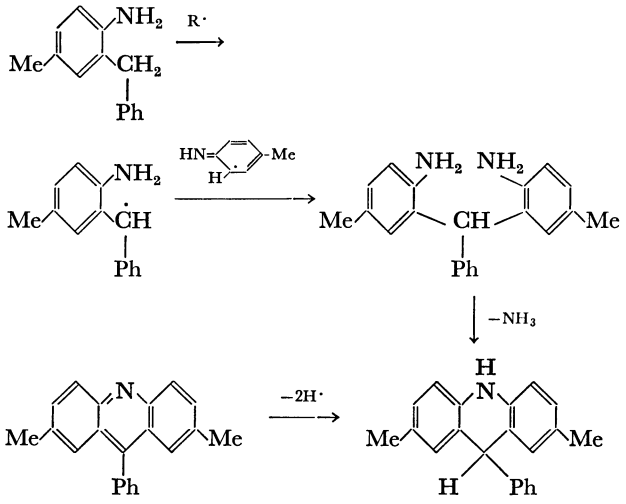
The general feature of this pyrolytic process appears to occur through a mechanism differing in nature from that induced by Lewis acid catalysis.[1]

The formation of toluene, bibenzyl, together with the corresponding toluidines and isomeric diphenylmethylindoles strongly suggests a free radical mechanism.

The homolytic character for the thermal pyrolysis of *N*-alkylarylamines was further confirmed through its study in high boiling solvents and the use of scavengers under nitrogen atmosphere. In phenol, the normal products of the amines rearrangements were obtained together with 2- and 4-benzylphenols. However, in anisole, which underwent preceding pyrolysis, *o*- and *p*-cresols were produced together with phenol, *o*- and *p*-benzylphenols.

The thermal rearrangement of each of *N*-benzyl-*o*- and *p*-toluidines in quinoline gave the normal rearrangement products together with 2- and 4-benzylquinolines, as summarized in Table 1.

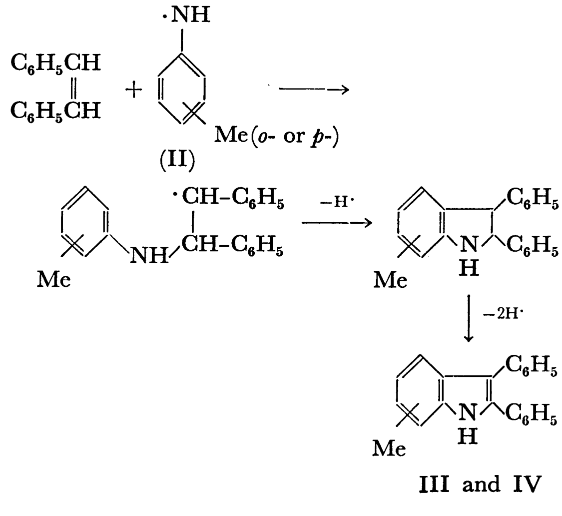
Coupling of benzyl radical (I) and toluidino radicals (II) produced the least stericaly hindered isomer, 3-methyl-4-aminodiphenylmethane, from *N*-benzyl-*o*-toluidine. However, from *N*-benzyl-*p*-toluidine, 2-amino-5-methyldiphenylmethane was not separated but most favorably consumed, after its preliminary production, into the formation of 2,7-dimethyl-9-phenylacridine as final product according to the following scheme.



Heating *o*- or *p*-toluidine alone in a sealed tube at about 315—330 °C for 12 days had resulted in the formation of ammonia.

Consequently, ammonia was assumed to be partially formed through intermediate formation of amino free radical[2] and tolyl radical as observed in isomeric toluidines pyrolysis under the rearrangement conditions.

The formation of both isomeric 2,3-diphenyl-7-methylindole (III) and 2,3-diphenyl-5-methylindole (IV) can be explained according to the following scheme:



III and IV

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Table 1. Products of pyrolysis of *N*-benzyl-*o*- and *p*-toluidines

Exp. No.	Condition: Solvent (g)	Condition: Temp (°C)	Condition: Time (day)	Amine (g): Isomer	Amine (g): Used	Amine (g): Consumed	Products (g): Ammonia	Products (g): Toluene	Products (g): Bibenzyl	Products (g): Stilbene	Products (g): Toluidine	Products (g): Benzyltoluidine	Products (g): Diphenylmethylindole	Products (g): Benzyl derivative
Bp/mmHg of fraction								110—112°C	118—125°C/5 mmHg		72—77°C/5 mmHg	155—158°C/4 mmHg	205—210°C/4 mmHg	
1		Reflux	46[e,i]	*o*-	40	28	Exist	0.08	0.2	Trace	5[b]	1.2[h]	1.5[f]	—
			15[e,ii]	*p*-	40	23	Exist	0.1	0.2	Trace	5[d]	—[m,i]	6.0[g]	—
2		330	12	*o*-	40	34	Exist	7.3	0.5	Trace	10[c]	1.1[h]	—	—
		315	12	*p*-	40	31	Exist	3.5	1.7	Trace	5.2[d]	—[m,ii]	1.0[g]	—
3[b]	Phenol (11)	330	12	*o*-	40	37	Exist	3.2	0.5	Trace	8[c]	1.3[h]	0.7[k]	3.1[l,i]
		315	12	*p*-	40	32	Exist	3.0	0.4	Trace	7[d]	—[m,iii]	3.0[g]	1.5[l,ii]
4[b]	Anisole(11)	330	12	*o*-	40	36	Exist	6.3	0.3	Trace	9[c]	4.0[h]	0.5[k]	—[i,i]
		315	12	*p*-	40	34	—[j]	3.5	0.1	Trace	6[d]	—[m,iv]	1.7[g]	—[i,ii]
5[b]	Quinoline(15)	330	12	*o*-	40	37	Exist	8.3	0.3	Trace	8[c]	1.8[h]	0.3[k]	1.5[n,i]
		315	12	*p*-	40	38	Exist	3.2	0.2	Trace	7[d]	—[m,v]	1.1	2.7[n,ii]

a) Benzyl derivative of solvent used. b) In nitrogen atmosphere. c) *o*-Toluidine. d) *p*-Toluidine. e) Benzaldehyde was separated and identified. (i) 0.7 g. (ii) 0.5 g. f) 2,3-Dimethyl-7-methylindole. g) 2,3-Diphenyl-5-methylindole. h) 4-Amino-3-methyldiphenylmethane. (i) Identified by paper chromatography as mixture of benzylphenols and by GLC analysis, (i) in ratio of (76.3%) *o*- and (23.7%) *p*-isomers; (ii) in ratio of (89.5%) *o*- and (10.5%) *p*-isomers. (j) Methylamine collected as hydrochloride salt. k) Colorless plates, mp 181—182 °C, IR spectrum showed an absorption at 3450 cm^{-1} (NH), not farther identified. l) Identified as phenols mixture, (i) yield (2.3 g.) in ratio of (67.3%) phenol and (32.7%) cresols, in ratio of *o*-cresol (95.7%) and *p*-cresol (4.3%), (ii) yield (1.1 g.) in ratio of (65.7%) phenol and (34.3%) cresols, in ratio of *o*-cresol (83.1%) and *p*-cresol (16.9%), together with benzylphenols (1.1 g) in ratio of (94.8%) *o*- and (5.2%) *p*-isomers. m) 2,7-Dimethyl-9-phenyl-acridine, collected at bp 230—240 °C/mmHg; M$^+$ *m/e* 283, (Found: C, 88.9; H, 6.2; N, 4.9%. Calcd for $C_{21}H_{17}N$: C, 89; H, 6; N, 5%) (i) 2.1 g, (ii) 0.7 g, (iii) 0.5 g, (iv) 1 g, (v) 0.2 g. n) Identified by TLC as mixture of 2- and 4-benzylquinolines and by GLC analysis to be (i) in ratio of (44%) 2- and (56%) 4-isomer, (ii) in ratio of (42%) 2- and (58%) 4-isomers.

trans-Stilbene could be resulted by radical abstraction of the methylene hydrogens from bibenzyl.

In anisole separation of *o*- and *p*-benzylphenols instead of benzylanisoles during amines rearrangement insures that anisole had rearranged under such conditions prior to substitution step by benzyl radical.

Migration of the methyl group of anisole was assumed to go through an intramolecular route, which was confirmed by absence of any other methyl derivative, together with the separation of higher yields of *o*-cresol. However, formation of *p*-cresol partially through an intermolecular migration of the methyl group within a solvent cage[3] could not be excluded.

Similarly, methylamine was expected to be formed intermolecularly, from *p*-toluidino radical and the methyl radical from anisole, through *N*-methyl-*p*-toluidine as preliminary product, which undergoes pyrolysis homolytically[4] into *p*-tolyl radical and methylamino radicals, the latter of which gives methylamine. However, methylamine formation was not observed in *N*-benzyl-*o*-toluidine pyrolysis with anisole.

Thermal rearrangement of either of *N*-benzyl-*o*- and -*p*-toluidines in quinoline gave the normal rearrangement products together with 2- and 4-benzylquinolines in a ratio similar to that obtained in the pyrolysis of benzyl naphthyl ethers[5] or *N*-benzyl-*N*-methylaniline[2] with quinoline as solvent, justifying the similarity in nature of all such types of rearrangements.

Experimental

Analysis. IR spectra were measured with a Pye-Unicam IR spectrophotometer, Model SP 200 g. The UV absorptions were carried out by a Pye-Unicam UV spectrophotometer, Model SP 8000. GLC analysis was carried out by a Pye-Unicam gas chromatograph, "series 104" dual flame ionization detector, temperature programed, Model 24. The column used was 20% SE 30 on chromosorb W (35—80 mesh). Thin layer chromatographic analysis of benzylquinolines was carried out on silica gel (25—40 mesh) using hexane–ethyl acetate (3: 7 by vol.); paper chromatographic analysis of benzylphenols was carried out using C. Schleicher and Schull paper No. 2816, using 1-butanol–water–ethanol mixture (5: 5: 1.7 by volume) as eluent. Mass spectral measurements were recorded on both, varian MAT CH-4, and AEI MS-9 mass spectrometers at 70 eV.

Pyrolysis of Each of N-*Benzyl*-o- *and* -p-*toluidines.* Heating each of *N*-benzyl-*o*-toluidine for 10 days at 320 °C and *N*-benzyl-*p*-toluidine for 10 days at 310 °C in sealed tubes, not resulted in their pyrolysis. However, heating each of the secondary amines at elevated temperatures and for the periods as specified in Table 1, either alone or with phenol, anisole or quinoline in nitrogen atmosphere and the reaction products were distilled first under atmospheric pressure where ammonia was evolved and trapped as its hydrochloride, and toluene collected. The higher boiling products were separated into neutral and amine fractions by treatment with concd HCl and extraction with ether.

Phenolic products were separated by means of Claisen's solution. The results are summarized in Table 1.

Preparation of Reference Compounds.

N-*Benzyl*-o-*toluidine*[6]: Bp 158—160 °C/5 mmHg; mp 56—57 °C.

N-*Benzyl*-p-*toluidine*[7]: Bp 160—162 °C/4 mmHg; n_D^{30}: 1.5985.

2-*Benzylphenol*[8]: Bp 170—180 °C/15 mmHg; phenylurethane derivative, mp 117 °C.

4-*Benzylphenol*[9]: Bp 170—180 °C/14 mmHg; mp 84 °C; benzoate, mp 87 °C.

2-*Benzylquinoline*[10]: Bp 235—240 °C/19 mmHg; picrate, mp 156—157 °C.

4-*Benzylquinoline*[11]. Bp 230 °C/17 mmHg; picrate, mp 178—179 °C.

trans-*Stilbene*[12]. Mp 123—124 °C.

Bibenzyl[13]. Mp 52—53 °C; 4,4′-dinitro derivative, mp 180 °C.

2,3-*Diphenyl*-5-*methylindole*[14]. Mp 153—154 °C.

2,3-*Diphenyl*-7-*methylindole*[15]. Mp 128—129 °C.

4-*Amino*-3-*methyl*-*diphenylmethane*[16]: Bp 160—162 °C, mp 63—64 °C; picrate, mp 181—182 °C, benzyl derivative, mp 135—136 °C.

2,7-*Dimethyl*-9-*acridine*[17]: Mp 171—172 °C; picrate, mp 267—268 °C.

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