Molecular Rearrangements, XV Photolysis and Thermolysis of N- α - and β -Phenethyl Toluidines

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Direct irradiation of each of N- α - and β -phenethyl toluidine in carbon tetrachloride solution leads to homolysis of the phenethyl-nitrogen bond forming phenethyl and aryl-amino free radicals. The fates of such radicals are discussed in terms of the identified products.

Thermolysis of the title compounds either alone or in presence of aromatic solvents such as isoquinoline or β -naphthol leads, in addition to the products obtained from photolysis, to partial attack of the so formed radicals on the solvent nuclei forming simple substitution products or polynuclear compounds of the indole, acridine and carbazole series.

N-Monoalkyl anilines or their hydrochlorides [1–4] were reported to rearrange on thermolysis into the corresponding ring alkylated products. Diphenylamines undergo pyrolysis [5] or photolysis [6] forming carbazoles. N,N-Dimethylaniline and its ethanolic solution were not significantly changed by ultraviolet irradiations, yet its acidified solution undergoes appreciable change on irradiation [7]. N-Benzylaniline has been reported to rearrange on irradiation [8] or heating [9, 10]. Similarly N-benzyl-*o*- or *p*-toluidines were found to undergo thermal rearrangement [11] and it was concluded that the pyrolysis of such secondary arylamines proceeds through a free radical intermolecular mechanism.

The present paper deals with the behaviour of some N-phenethyl toluidines either on photolysis or thermolysis.

The non-catalysed ultraviolet irradiation of N-(α -phenethyl)*o*-toluidine in the non-polar aprotic solvent carbon tetrachloride leads to the formation of ethylbenzene, 2,3-diphenylbutane and 2,3-diphenylbutene as neutral products together with *o*-toluidine, 4(α -phenethyl)*o*-toluidine and 2(α -phenethyl)*o*-toluidine.

N(α -phenethyl)*p*-toluidine under the same photolytic conditions gives the same neutral products in addition to *p*-toluidine and 2(α -phenethyl)*p*-toluidine.

The process appears to involve the preliminary homolysis of the alkyl-N bond leading to the formation of α -phenethyl and the corresponding toluidino free radicals. Hydrogen abstraction by the α -

phenethyl radicals gives ethylbenzene while their dimerisation gives rise to 2,3-diphenylbutane which may be dehydrogenated under the influence of the free radicals present in the reaction medium forming 2,3-diphenylbutene. On the other hand, the toluidino radicals abstract hydrogen forming the corresponding toluidine or couples with α -phenethyl free radicals forming C-alkylated derivatives of toluidines namely; 2- or 4(α -phenethyl)*o*-toluidine in case of *o*-toluidine and 2(α -phenethyl)*p*-toluidine in case of *p*-toluidine. Both 2(α -phenethyl)*o*-toluidine and its 4-isomer are stable under such photolytic conditions, therefore neither is an intermediate in the formation of the other, but they are formed as primary substitution products as represented by the following Scheme 1.

Scheme 1.

Similarly, photolysis of N(β -phenethyl)*o*-toluidine and its *p*-isomer under the same conditions gives rise to the previous products in addition to a low yield of 1,4-diphenylbutane. Therefore, it seems that the β -phenethyl free radicals formed during photolysis undergo isomerisation to their most

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stable α -counterparts as observed in a previous work [12] that subsequently participates in the formation of the identified products.

The behaviour of such secondary amines on thermolysis was also studied. Thus, refluxing *N*(α -phenethyl)*o*-toluidine in air for 9 days gives rise to ammonia, toluene, ethylbenzene, acetophenone, 2,3-diphenylbutane, 2,3-diphenylbutene, *o*-toluidine, and 4(α -phenethyl)*o*-toluidine together with 4,9-dimethylacridine. When the thermolysis was carried out in a sealed tube under nitrogen atmosphere, the previous products were obtained except acetophenone while 3-phenyl-7-methylindole was identified among the products. When the pyrolysis was affected in presence of isoquinoline as an aromatic solvent, 1(α -phenethyl)isoquinoline was identified among the products.

Similarly in presence of β -naphthol, in addition to the normal pyrolysis products, 1(α -phenethyl)-2-naphthol and 8,9-dimethyl-9-phenyl-3,4-benzoacridan were also obtained. Similar results were also obtained on pyrolysis of *N*(α -phenethyl)*p*-toluidine whereby toluene, ethylbenzene, 2,3-diphenylbutane, 2,3-diphenylbutene, *p*-toluidine, 2(α -phenethyl)*p*-toluidine and 3,6-dimethylcarbazole were formed.

In presence of β -naphthol, the usual rearrangement products were accompanied by the formation of 6,9-dimethyl-9-phenyl-3,4-benzoacridan.

In presence of isoquinoline, which acts as an effective radical scavenger, the β -phenethyl radicals were captured as soon as they are formed forming 1(β -phenethyl)isoquinoline while no 1(α -phenethyl)isoquinoline could be detected among the products. Moreover, in presence of such radical scavenger, the yield of ethylbenzene and the attack of phenethyl radicals on the toluidine moiety is greatly reduced (*cf.* Table II).

The main feature of all such *N*-phenethyltoluidines rearrangements is the homolysis of the phenethyl-nitrogen bond forming toluidino and α - or β -phenethyl free radicals. The normal fate of such radicals is the same as in photolysis. Moreover, the toluidines obtained may also undergo secondary pyrolytic process through deamination as reported before [13] to form finally toluene and ammonia.

The formation of acetophenone from α -phenethyl radicals is due to their trapping by atmospheric oxygen as described for the formation of benzaldehyde from benzyl radicals [14].

2(α -Phenethyl)*o*-toluidine may be supposed to be the precursor of 4,9-dimethylacridine through cyclisation followed by dehydrogenation:

Infrared absorption spectrum of 4,9-dimethylacridine shows neither NH_2 nor NH characteristic bands but instead exhibits $\nu\text{C}=\text{N}$ characteristic for tertiary arylamines at 1370 cm^{-1} . Its electronic absorption spectrum shows absorption maxima at 255 nm ($\epsilon\ 172,000$) and 322 nm ($\epsilon\ 5,600$) characteristic for acridine moiety [14].

3-Phenyl-7-methylindole can rationally be assumed to take place through the following steps:

The styrene adds on *o*-toluidine radical followed by cyclisation and finally dehydrogenation.

Such indole structure was further ascertained by its IR spectrum which shows $\nu\text{N-H}$ at 3400 cm^{-1} . Its electronic absorption shows absorption maxima at 272 nm ($\epsilon\ 2680$) and 285 nm ($\epsilon\ 1920$) characteristic for indole moiety [15]. The formation of 3,6-dimethylcarbazole was assumed to proceed through dimerization of the mesomeric *p*-toluidino radicals followed by cyclisation through elimination of ammonia.

8,9-Dimethyl-9-phenyl-3,4-benzoacridan and 6,9-dimethyl-9-phenyl-3,4-benzoacridan can be presumably formed through the attack of 2(α -phenethyl)*o*-toluidino or 2(α -phenethyl)*p*-toluidino radicals on the α -position of β -naphthol followed by elimination of water.

Their molecular structures were further confirmed by elemental analysis together with their spectral data. The infrared absorption spectra show ν_{NH} at 3400 cm^{-1} and their electronic absorption spectra show absorption maxima at 254 nm ($\epsilon\ 170,000$) and 315 nm ($\epsilon\ 6,800$) indicating the presence of acridine nucleus [15].

Experimental

All m.p.s. are uncorrected. The IR spectroscopic analyses were carried out on a Pye-Unicam IR spectrophotometer, Model SP. 200 G. The u.v. absorptions were carried out using a Pye-Unicam UV spectrophotometer, Model SP 8000. G. L. C. was carried out using a Pye-Unicam gas chromatograph Series 104, Dual flame ionisation detector, Model 24 and the column used was 20% SE 30 on chromosorb W (35–80 mesh) at temperature 185°C using nitrogen as a carrier gas. Molecular weight determination of some reaction products was carried out by mass spectrophotometer, Model A.E.I. M.S. 902. Ultra-violet irradiation was carried out using Mallinkrodt 150 W mercury discharge lamp and the solutions were contained in open topped pyrex beakers.

Photolysis of *N*-phenethyl toluidines

The amine (1 g) dissolved in dry carbon tetrachloride (10 ml) was irradiated for 15 h at room temperature (25°C). The photolysate was separated as indicated in previous work [10] into amine and neutral products and analysed by g.l.c. The results are summarized in Table I.

Thermolysis of *N*-phenethyl toluidines

The amine was heated under reflux in air or in sealed tubes in nitrogen atmosphere at $310\text{--}315^\circ\text{C}$ for about 9 days either alone or in presence of aromatic solvents such as β -naphthol or isoquinoline. The ammonia evolved was identified through the formation of its hydrochloride by absorption in a trap containing hydrochloric acid. The products were separated as usual and identified by t.l.c., g.l.c.; UV, IR and mass spectroscopy or mixed m.p. with authentic samples whenever possible as summarized in Tables II and III.

Preparation of reference compounds

- N*-(α -phenethyl)-*o*-toluidine [8]: colourless crystals from petroleum ether ($40\text{--}60^\circ\text{C}$), m.p. $31\text{--}32^\circ\text{C}$, b.p. $145\text{--}148^\circ\text{C}/8\text{ mm Hg}$.
N-(α -phenethyl)-*p*-toluidine [16]: cryst. from petroleum ether ($40\text{--}60^\circ\text{C}$), b.p. $155\text{--}160^\circ\text{C}/5\text{ mm Hg}$, m.p. $70\text{--}71^\circ\text{C}$.
N-(β -phenethyl)-*o*-toluidine [17]: colourless oil, b.p. $167\text{--}170^\circ\text{C}/6\text{ mm Hg}$ $n_D^{25}\ 1.5892$.
N-(β -phenethyl)-*p*-toluidine [17]: cryst. from petroleum ether ($40\text{--}60^\circ\text{C}$), m.p. $25\text{--}26^\circ\text{C}$, b.p. 153 to $155^\circ\text{C}/2\text{ mm Hg}$.
2,3-Diphenylbutane [18]: cryst. from ethanol m.p. $123\text{--}124^\circ\text{C}$;
2,3-diphenylbutene [19]: cryst. from ethanol m.p. 66°C ;
1,4-diphenylbutane [20]: colourless oil b.p. 140 to $142^\circ\text{C}/15\text{ mm Hg}$;
1-(α -phenethyl)-2-naphthol [21]: oil b.p. 245 to $250^\circ\text{C}/4\text{ mm Hg}$; benzoate m.p. 132°C ;
1-(α -phenethyl)-isoquinoline [22]: b.p. $160\text{--}170^\circ\text{C}/10\text{ mm Hg}$; $n_D^{20}\ 1.6428$;
1-(β -phenethyl)-isoquinoline [23]: b.p. $190\text{--}193^\circ\text{C}/3\text{ mm Hg}$; $n_D^{20}\ 1.6200$, picrate m.p. $189\text{--}191^\circ\text{C}$;
2-(α -phenethyl)-*p*-toluidine [16]: b.p. $178\text{--}181^\circ\text{C}/15\text{ mm}$; picrate m.p. $165\text{--}167^\circ\text{C}$;
4-(α -phenethyl)-*o*-toluidine [16]: cryst. from petroleum ether ($40\text{--}60^\circ\text{C}$) m.p. $55\text{--}56^\circ\text{C}$; picrate m.p. $174\text{--}176^\circ\text{C}$;
3,6-dimethylcarbazole [24]: cryst. from benzene m.p. $219\text{--}222^\circ\text{C}$, picrate m.p. 195°C .

Table I. Percentage composition of *N*-phenethyl toluidines photolysates.

	<i>N</i> -(α -phenethyl)- <i>o</i> -toluidine	<i>N</i> -(α -phenethyl)- <i>p</i> -toluidine	<i>N</i> -(β -phenethyl)- <i>o</i> -toluidine	<i>N</i> -(β -phenethyl)- <i>p</i> -toluidine
Ethylbenzene	32.8	29.7	4.5	2.5
2,3-Diphenylbutane	14.8	13.3	37.9	41.4
2,3-Diphenylbutene	2.4	7.0	6.0	3.8
1,4-Diphenylbutane	—	—	1.5	2.3
Toluidine	6.2	7.1	29.5	18.5
Phenethyl toluidine	37.6 ^a	33.0	13.2 ^b	9.8
Unchanged amine	6.2	9.9	7.4	21.7

^a 2-(α -Phenethyl)-*o*-toluidine and its 4-isomer in the ratio 1:12.5.

^b 2-(α -Phenethyl)-*o*-toluidine and its 4-isomer in the ratio 1:5.

Tab. II. Products of pyrolysis of N(α - or β -phenethyl)*o*-toluidine.

Expt. No.			1	2	3	4	5	6	7
Solvent			—	—	β -Naphthol	isoquinoline ¹	—	β -Naphthol	isoquinoline
Temp. [°C]/time [d]			reflux/9 in air	350/6	350/7	350/4	350/9	350/9	350/9
Amount of amine consumed/used [g]			42/42	34/36	17/28	22/28	26/35	20/24	18/27
Products [g, %]	b.p. [°C/Torr]	m.p. [°C]							
Toluene ^a	110/760	—	1.5 (3.58)	1.3 (3.8)	2.1(12.35)	0.8 (3.63)	8.8 (3.07)	0.8 (4.0)	0.2 (1.12)
Ethylbenzene ^b	130/760	—	3.5 (8.34)	3.3 (9.7)	2.5(14.7)	2.8 (12.72)	2.1 (8.07)	2.5 (12.50)	0.7 (3.89)
Acetophenone ^c	65–70/3	—	0.7 (1.67)	—	—	—	—	—	—
2,3-Diphenylbutane } 2,3-Diphenylbutene } 1,4-Diphenylbutane }	123–124 135–150/3 ^d	66	1.2 (2.86) 2.3 (5.48)	1.4 (4.12) 1.8 (5.29)	0.5 (2.94) 1.2 (7.05)	1.06 (4.81) 1.44 (6.55)	1.32 (5.07) 0.44 (1.69)	1.25 (6.25) 0.8 (4.0)	0.23 (1.28) 0.30 (1.67)
3-Phenyl-7-methylindole ^e	165–180/3	186–188	2.1 (5)	3.5 (9.8)	—	4.5 (20.45)	2.8 (10.76)	—	1.8 (10)
<i>o</i> -Toluidine ^f	72–75/3	—	11 (26.19)	9.5(10.29)	3.5(20.6)	8.8 (40)	7.5 (28.84)	3.5 (17.5)	6.7 (37.23)
4-(α -Phenethyl) <i>o</i> -toluidine ^h	170–180/3	55–56	1 (2.38)	2.2 (6.47)	1 (5.9)	1 (4.55)	5 (19.23)	5 (25)	1.1 (6.12)
4,9-Dimethylacridine } Alkyl deriv. of solvent } Other products }	80–81	—	1 (2.38)	2.3 (6.76)	1 (5.9)	—	2.3 (8.84)	—	—
	—	—	—	—	1 (8) ⁱ	1 (45.45) ^m	—	0.5 (2.5) ⁱ	9 ⁿ
	—	—	—	—	j, k	—	—	j, k	—

Table III. Products of pyrolysis of N(α - or β -phenethyl)*p*-toluidine.

Expt. No.			1	2	3	4	5	6	7
Solvent			—	—	β -Naphthol	isoquinoline ^s	—	β -Naphthol	isoquinoline
Temp. [°C]/time [d]			reflux. in air/15	350/10	350/7	350/5	350/15	350/8	350/9
Amount of amine, consumed/used [g]			25/35	32/36	28/30	26/29	19/36	21/25	26/29
Products [g]	b.p. [°C/Torr]	m.p. [°C]							
Toluene ^a	110/760	—	0.5 (2)	0.7 (2.19)	1.8 (6.43)	1.3 (5)	0.2 (1.05)	1.2 (5.72)	0.5 (1.93)
Ethylbenzene ^b	130/760	—	1.2 (4.8)	3.0 (9.38)	3.0(10.72)	3.6 (13.85)	0.5 (2.63)	3.1 (14.77)	0.8 (3.08)
Acetophenone ^c	65–70/3	—	0.4 (1.6)	—	—	—	—	—	—
2,3-Diphenylbutane } 2,3-Diphenylbutene } 1,4-Diphenylbutane }	123–124 135–150/3 ^d	66	1.1 (4.4) 0.7 (2.8)	1.2 (3.75) 0.8 (2.5)	0.46 (1.65) 1.24 (4.43)	0.44 (1.70) 0.56 (2.16)	0.68 (3.58) 0.98 (5.16)	6.24(29.72) 0.18 (0.86)	0.10 (0.39) 0.43 (1.66)
3,6-Dimethylcarbazole ^o	200–210/3	219–222	0.7 (2.8)	1.8 (5.63)	—	2.5 (9.62)	—	—	—
<i>p</i> -Toluidine ^f	70–75/3	45–46	4.0 (1.6)	9.5(29.69)	4 (14.29)	9 (34.62)	3.3 (17.37)	4.8 (22.86)	9 (34.62)
2(α -Phenethyl) <i>p</i> -toluidine ^p	170–180/3	—	6.0(24)	3.2(10)	1.8 (6.43)	2.3 (8.85)	2 (10.53)	1.5 (7.15)	2.2 (8.47)
Alkyl deriv. of solvent	—	—	—	—	0.7 (7) ⁱ	1.3 (40.62) ^m	—	0.5 (5) ⁱ	8.5 (32.7) ^t
Other products	—	—	1.2 (4.8) ^q	2 (6.25) ^q	12 (42.86) ^r	2 (7.7) ^q	2 (10.53) ^q	9 (42.86) ^r	—

Expts. 1–4 using N(α -phenethyl)*o*- or *p*-toluidine. Expts. 5–7 using N(β -phenethyl)*o*- or *p*-toluidine.

^a 2,4-Dinitro deriv. m.p. and mixed m.p. 72–73 °C; ^b on oxidation gives benzoic acid m.p. 122 °C; ^c D.N.P. deriv. m.p. and mixed m.p. 250 °C; ^d Identified and estimated by g.l.c. as compared with authentic samples; ^e Analysis: found C 86.80, H 5.98, N 6.88; calc. C 86.92, H 6.32, N 6.75%; ^f benzoyl deriv. m.p. and mixed m.p. 144–145 °C; ^h separated from such fraction by column chromatography over silica gel (80–120 mesh) and eluted with petrol ether (60–80 °C); m.p. and mixed m.p. 55–56 °C; picrate m.p. and mixed m.p. 174–176 °C; ⁱ Calc. on basis of β -naphthol consumed; 1(α -phenethyl)2-naphthol, b.p. 245–250 °C/4 Torr; benzoate m.p. and mixed m.p. 132 °C; ^j 8,9-dimethyl-9-phenyl-3,4-benzoacridan, b.p. 230–250 °C/5 Torr; (6 g) purified through picrate formation m.p. 156–158 °C and its structure is based on elemental, spectral and molecular ion determination, together with water (0.6 g) separation; ^k tertiary nitrogen compound (4.5 g), b.p. 200–220 °C/4 Torr; m.p. 123–125 °C; picrate 263–265 °C; elemental and molecular weight data conforms to the structure C₁₇H₁₃N. ^l amount consumed/used, in g 2.2/8.6; ^m Calc. on basis of isoquinoline consumed, 1(α -phenethyl)isoquinoline, b.p. 160–170 °C/10 Torr, n_D^{20} 1.6428; ⁿ consists mainly of 1(β -phenethyl)isoquinoline b.p. 190–192 °C/3 Torr, n_D^{20} 1.6200; picrate m.p. and mixed m.p. 189–191 °C together with traces of α -isomer as shown by t.l.c.; ^o b.p. 220–230 °C/3 Torr, m.p. and mixed m.p. 219–222 °C; picrate m.p. and mixed m.p. 195 °C; ^p picrate m.p. and mixed m.p. 165–167 °C; ^q unknown tertiary nitrogen compound b.p. 200–220 °C/3 Torr, m.p. 127–128 °C, picrate m.p. 198–200 °C; ^r 6,9-dimethyl-9-phenyl-3,4-benzoacridan, m.p. 95–96 °C, picrate m.p. 110–112 °C, identified through elemental, spectral analyses and molecular ion determination, together with water (0.5 g) separation; ^s amount consumed/used in g 3.2/8.8; ^t 1(β -phenethyl)isoquinoline, b.p. 190–192 °C/3 Torr, n_D^{20} 1.6270, purified through picrate formation m.p. and mixed m.p. 189–191 °C.

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