669. *Molecular Rearrangement of Tertiary Amines. Part II.**

By R. A. W. Johnstone and T. S. Stevens.

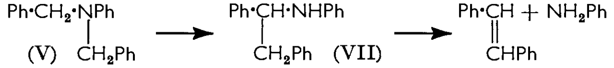
The rearrangement reported in Part I has been extended to other tertiary amines and has been shown to be intramolecular. The process has been applied for a new synthesis of phenanthrene.

It was shown earlier [1] that rearrangement of quaternary ammonium salts is intramolecular and it is now shown that this is true of the rearrangement of a tertiary amine. *N*-Benzyl-*N*-phenacylaniline (I), having the benzyl group radioactively labelled, was rearranged along with an inactive amine, *N*-benzylanilinomethyl t-butyl ketone (II). When the products (III) and (IV) were separated, all the radioactivity appeared in the former, so that the migrating radical could not have been free at any time during the reaction. Qualitatively, the compounds (I) and (II) rearrange with comparable facility (Part I).

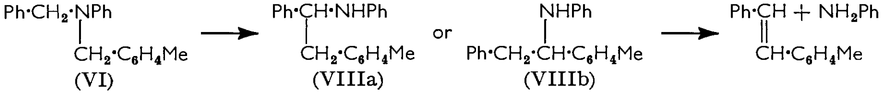
$$\text{(I)}\quad \mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}NPh{\cdot}{}^{14}CH_2Ph} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}CH(NHPh){\cdot}{}^{14}CH_2Ph}\quad \text{(III)}$$

$$\text{(II)}\quad \mathrm{Bu^t{\cdot}CO{\cdot}CH_2{\cdot}NPh{\cdot}CH_2Ph} \longrightarrow \mathrm{Bu^t{\cdot}CO{\cdot}CH(NHPh){\cdot}CH_2Ph}\quad \text{(IV)}$$

Confirmation came from experiments with dibenzylaniline (V) and its 4-methyl derivative (VI). Under the severe conditions necessary for rearrangement, the expected secondary amines (VII) and (VIIIa or VIIIb) undergo β-elimination, yielding aniline and a derivative of stilbene.



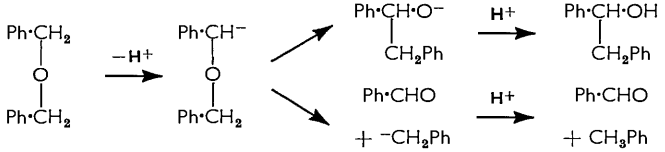
$$\text{(V)}\ \mathrm{Ph{\cdot}CH_2{\cdot}N(Ph){\cdot}CH_2Ph} \longrightarrow \mathrm{Ph{\cdot}CH(NHPh){\cdot}CH_2Ph}\ \text{(VII)} \longrightarrow \mathrm{Ph{\cdot}CH{=}CHPh} + \mathrm{NH_2Ph}$$



$$\mathrm{Ph{\cdot}CH_2{\cdot}N(Ph){\cdot}CH_2{\cdot}C_6H_4Me}\ \text{(VI)} \longrightarrow \mathrm{Ph{\cdot}CH(NHPh){\cdot}CH_2{\cdot}C_6H_4Me}\ \text{(VIIIa)}\ \text{or}\ \mathrm{Ph{\cdot}CH_2{\cdot}CH(NHPh){\cdot}C_6H_4Me}\ \text{(VIIIb)} \longrightarrow \mathrm{Ph{\cdot}CH{=}CH{\cdot}C_6H_4Me} + \mathrm{NH_2Ph}$$

The crude product from the example (VI) gave, on bromination, methylstilbene dibromide, with none of the dibromide of stilbene and of dimethylstilbene to be expected if the reaction had been intermolecular.

Rearrangement of ethers [2] is accompanied by a fission which may be formulated:



$$\mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}Ph} \xrightarrow{-\mathrm{H^+}} \mathrm{Ph{\cdot}CH^-{\cdot}O{\cdot}CH_2{\cdot}Ph} \nearrow \mathrm{Ph{\cdot}CH(O^-){\cdot}CH_2Ph} \xrightarrow{\mathrm{H^+}} \mathrm{Ph{\cdot}CH(OH){\cdot}CH_2Ph};\quad \searrow \mathrm{Ph{\cdot}CHO} + {}^-\mathrm{CH_2Ph} \xrightarrow{\mathrm{H^+}} \mathrm{Ph{\cdot}CHO} + \mathrm{CH_3Ph}$$

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* Part I, preceding paper.

[1] Johnstone and Stevens, *J.*, 1955, 4487.

[2] Wittig and Happe, *Annalen*, 1947, **557**, 205.

In the degradation of quaternary ammonium salts similar fission occurs to only a small extent, if at all, whereas with some tertiary amines it plays such a large part that little or no rearrangement can be detected. These contrasts are intelligible in terms of the changes in covalency which occur at the decisive stages of the alternative processes. In the rearrangement of an ammonium salt the passage of the nitrogen atom from the quadricovalent to the tercovalent state presents little energetic difficulty, while rearrangement of an ether or an amine requires reduction of the normal covalency of oxygen or nitrogen, with assumption of an anionic charge. This will be easier for an ether, and in the series R_4N^+, R_2O, R_3N, rearrangement becomes progressively more difficult and fission tends to dominate. These reactions depend on the extraction of a proton by a basic reagent, which meets increasing resistance in the series $(Ph\cdot CH_2)_2NR_2^+$, $(Ph\cdot CH_2)_2O$, $(Ph\cdot CH_2)_2NR$.

Case *	Reagent	Temp.	Time (hr.)	Products
A,† $X\cdot NPh\cdot CH_2Ph$	NaOH	300°	2	Toluene (~5%); little $NHPh\cdot CH_2Ph$ & fluorenone anil
	$KOBu^t$	170	3	Much A recovd.; little $NHPh\cdot CH_2Ph$; NH_2Ph after hydrolysis.
	$NaNH_2$	200		Trace PhMe, bifluorenyl.
	MeLi	240	0·5	Tar.
	PhLi	110—130		Tar; biphenyl.
	K in boiling decalin		4	Tar.
B, $X\cdot NPh\cdot CH_2\cdot CH:CH_2$	KOH	120—135	1	Some B recovd.; biphenyl-2-carboxylic acid (5%); fluorenoneanil (11%); *N*-phenyl-9-fluorenylamine (7%); allylaniline (12%).
C,† $X\cdot NMe\cdot CH_2Ph$	KOH	140	3	80% C recovd.; fluorenone; biphenyl-2-carboxylic acid.
	NaOH	295	2	Bifluorenyl; no toluene; tar.
	$KOBu^t$	170	3	9-Fluorenylamine (16%); fluorenone.
	$NaNH_2$	250	1·5	Same + PhMe (15%).
	MeLi	200		Tar.
	PhLi	200		Amorphous products.
D,[3] $NMeX_2$	KOH	200		Fluorene (10%); bifluorenyl (8%).
E, $X\cdot N(CH_2Ph)_2$	$KOBu^t$	170	2	9-Fluorenylamine (40%); Ph·CHO; no stilbene.
F, $Ph_2CH\cdot NMe\cdot CH_2Ph$	$NaNH_2$	260	2·5	CH_2Ph_2 (3%); PhMe (~10%); Ph·CH:NMe (~8%).
G, $(Ph\cdot CH_2)_2NPh$	KOH	280	0·5	80% G recovd.; PhMe; Ph·CH:NMe.
	$NaNH_2$	250—270	1·5	Much Ph·CH:NMe; PhMe (>20%); stilbene (8%); BzOH (10%).
H, $\begin{array}{l} Ph\cdot CH_2\cdot NPh \\ \qquad\quad \vert \\ Me\cdot C_6H_4\cdot CH_2 \end{array}$	$NaNH_2$	260	1·5	PhMe (50—60%); *p*-xylene (50—60%); 4-methylstilbene (~6%); NH_2Ph after hydrolysis.
I,[4] $(Ph\cdot CH_2)_2NMe$	$NaNH_2$	260—270	2	PhMe (~15%); Ph·CH:NMe (~15%) stilbene (1%).
J,[5] $\begin{array}{l} Ph\cdot CH_2\cdot NMe \\ \qquad\quad \vert \\ Me\cdot C_6H_4\cdot CH_2 \end{array}$	$NaNH_2$	230—240	1·25	Much PhMe and *p*-xylene; 4-methylstilbene (~1%).

Substances were in general identified by mixed m. p.s. In individual cases: toluene as 2,4-dinitrotoluene; benzylaniline as benzoyl derivative; fluorenone as 2,4-dinitrophenylhydrazone; aniline as benzanilide, tribromoaniline, or benzeneazo-β-naphthol; fluorenone anil by inference from the products of its acid hydrolysis; allylaniline as oxalate; 9-fluorenylamine as hydrochloride, picrate, and benzoyl derivative;[6] benzaldehyde as 2,4-dinitrophenylhydrazone; diphenylmethane as 2,4,2′,4′-tetranitroderivative; benzylidenemethylamine and benzylideneaniline from the products of hydrolysis; stilbene as dibromide; *p*-xylene as trinitro-*p*-xylene; 4-methylstilbene as dibromide.[7]

* X = 9-Fluorenyl.

† Several experiments on the compounds A and C were carried out by Dr. S. F. Marrian (Thesis, Glasgow, 1941).

The behaviour of a variety of tertiary amines is summarised in the Table. The fluorenyl radical contains a proton almost as mobile as that of the phenacyl group present in the

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[3] Bamford, Stevens, and Wright, *J.*, 1952, 4334.

[4] Goss, Ingold, and Wilson, *J.*, 1926, 2457.

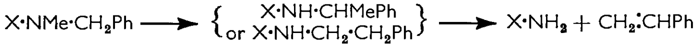
[5] von Braun and Engel, *Annalen*, 1924, **436**, 309.

[6] Schmidt and Stützel, *Ber.*, 1908, **41**, 1243.

[7] Anschütz, *Ber.*, 1885, **18**, 1946.

amines discussed in Part I, but in none of the five cases studied could migration from the nitrogen atom to the fluorene nucleus be effected. In case A several unsuccessful attempts were made to synthesise the expected product of rearrangement, 9-benzyl-*N*-phenylfluorenylamine; here a marked overcrowding of groups is indicated by the impossibility of constructing a model (Courtauld) of the secondary base. This overcrowding effect would not be expected to hinder to the same extent the rearrangement of *N*-allyl-9-fluorenylaniline, but this compound (case B) suffered extensive decomposition under relatively mild conditions.

The formation of 9-fluorenylamine in case C is surprising. It can be explained by assuming migration of the methyl into the benzyl group, or *vice versa*, with subsequent β-elimination:



$$\mathrm{X{\cdot}NMe{\cdot}CH_2Ph} \longrightarrow \left\{\begin{matrix}\mathrm{X{\cdot}NH{\cdot}CHMePh}\\ \text{or } \mathrm{X{\cdot}NH{\cdot}CH_2{\cdot}CH_2Ph}\end{matrix}\right\} \longrightarrow \mathrm{X{\cdot}NH_2 + CH_2{:}CHPh}$$

(X = 9-Fluorenyl)

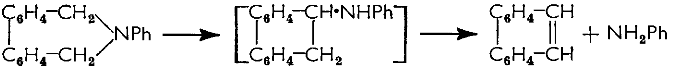
Both postulated intermediates have been synthesised and shown to yield 9-fluorenylamine under the conditions of the attempted rearrangement. In case E, however, where fluorenylamine was again produced, the easily recognised stilbene could not be detected.

N-Diphenylmethyl-*N*-methylbenzylamine (F) gave indication of fission, but no evidence of rearrangement.

Tertiary dibenzylamines (G, H, I, J) (cf. formula V) alone showed strong evidence of rearrangement in addition to fission. The bases G and H gave some 8% of stilbene derivative, but bases I and J gave only 1%; *N*-arylation had the expected effect of promoting rearrangement.

The compound (IX) presents a favourable case for rearrangement, here involving ring-contraction. With sodamide at 250° it gave aniline and some 40% of phenanthrene; under these conditions it was to be expected that β-elimination should follow rearrangement.

(IX)



EXPERIMENTAL

[α-^{14}C]*Benzylaniline.*—Aniline (1 ml.), water (0·3 ml.), and sodium hydrogen carbonate (250 mg.) were stirred at 90° and [^{14}C]benzyl chloride [1] (200 mg.) was added during 1 hr. The mixture was heated for 3 hr. more, cooled, and extracted with ether, and the extract was dried (Na_2SO_4) and evaporated. The residue was heated at 100°/10 mm. to remove aniline. Distillation yielded [^{14}C]benzylaniline (150 mg.), b. p. 200° (bath)/10 mm.

([α-^{14}C]*Benzyl*)*phenacylaniline* (I).—[α-^{14}C]Benzylaniline (300 mg.), phenacyl bromide (325 mg.), and sodium hydrogen carbonate were stirred in ethanol (2 ml.) for 3 hr. at 60°. The mixture was treated with water (25 ml.) and ether, the ether layer was washed with dilute hydrochloric acid and water, and dried (Na_2SO_4), and the residue (I) obtained on evaporation, crystallised from ethanol; it had m. p. 109° alone or mixed with a non-radioactive specimen (Part I).

4-*Methylbenzyl Bromide.*—*p*-Xylene (1·25 mols.) and *N*-bromosuccinimide (1 mol.) were refluxed in carbon tetrachloride with a little dibenzoyl peroxide. After 20 min. the mixture was filtered from succinimide and distilled, giving an almost quantitative yield of bromide, b. p. 120°/15 mm.

The bases tabulated were prepared from 9-bromofluorene, 4-methylbenzyl bromide, or diphenylmethyl bromide, with the appropriate secondary amine by reaction of (*a*) amine (2 mols.) and halide (1 mol.) in benzene, or (*b*) amine (1 mol.) and halide (1 mol.) in methanol with solid sodium hydrogen carbonate. Base F was precipitated by 5N-hydrochloric acid as the hydrochloride, which was crystallised from ethanol and 2N-hydrochloric acid.

N-(α-*Methylbenzyl*)-9-*fluorenylamine*, prepared similarly to compound (A), crystallised from ethanol in prisms, m. p. 64—66° (Found: C, 88·5; H, 6·9; N, 5·1. $C_{21}H_{19}N$ requires C, 88·5; H, 6·7; N, 4·9%).

9-Bromofluorene and phenethylamine gave, as in case (F), N-*phenethyl*-9-*fluorenylamine hydrochloride*, needles, m. p. 222—224° (Found: C, 78·5; H, 6·2; N, 4·4; Cl, 11·1. $C_{21}H_{20}NCl$ requires C, 78·4; H, 6·2; N, 4·4; Cl, 11·0%). The oily base gave a *benzoyl derivative*, rectangular plates (from ethanol), m. p. 149—150° (Found: C, 86·5; H, 6·1; N, 3·6. $C_{28}H_{23}ON$ requires C, 86·4; H, 5·9; N, 3·6%). When 9-bromofluorene (1 mol.) and phenethylamine (1 mol.) were refluxed in acetonitrile for 2 hr., an initial precipitate soon redissolved, and N-*phenethyldi*-9-*fluorenylamine* crystallised on cooling; this had m. p. 180—181° (from ethanol) (Found: C, 90·9; H, 6·0; N, 3·1. $C_{34}H_{27}N$ requires C, 90·9; H, 6·0; N, 3·1%).

			Time			Found (%)				Required (%)		
Base *	Method	Temp.	(hr.)	Solvent	M. p.	C	H	N	Formula	C	H	N
A	*a*	15°	18	C_6H_6–MeOH	144°	—	—	4·2	$C_{26}H_{21}N$	—	—	4·0
B	*b*	70	30	EtOH	98—102	88·5	6·5	4·8	$C_{22}H_{19}N$	88·8	6·4	4·7
C [a]	*a*	15	18	MeOH	87—89	—	—	5·2	$C_{21}H_{19}N$	—	—	4·9
E	*a*	85	10	C_6H_6–EtOH	125—126	90·0	6·7	3·7	$C_{27}H_{23}N$	89·9	6·4	3·9
F [b]	*a*	85	2		218—221	(HCl, 11·2)			$C_{21}H_{22}NCl$	(HCl, 11·3)		
H	*b* [c]	80	6	EtOH	79—80	87·7	7·3	4·9	$C_{21}H_{21}N$	87·7	7·3	4·9
J	*a*	15	48	—	[d]	85·6	8·5	6·3	$C_{16}H_{19}N$	85·3	8·4	6·3

* For symbolism see Table on p. 3347.

[a] *Picrate*, prisms (from ethanol), m. p. 163—164° (Found: N, 10·9. $C_{27}H_{22}O_7N_4$ requires N, 10·9%). [b] Hydrochloride. [c] Prepared in water–benzene, not methanol. [d] B. p. 107°/10 mm.

Mechanism of Rearrangement.—The compounds (I) (100 mg.) and (II) (100 mg.) were fused with potassium hydroxide (1 g.) at 150° for 45 min. under nitrogen, and the mixture dissolved in ligroin (b. p. 60—80°) and water. The organic layer, washed with water, was stirred with 8N-hydrochloric acid, and the precipitate (P) collected on a sintered-glass filter. The acidic layer in the filtrate was washed with ether and basified, precipitating base (Q). On being washed with ether and decomposed with dilute sodium hydroxide solution, material (P) gave a yellow solid which, thrice crystallised from ligroin (b. p. 60—80°), had m. p. 105°, alone or admixed with base (III). The base (Q) was similarly purified and identified with base (IV), m. p. 123°. Samples of materials (I), (III), and (IV) were matted on small metal planchettes, and their radioactivity was measured at infinite thickness by a Geiger–Müller end-window counter:

Compound	None	(I)	(III)	(IV)
Counts min.$^{-1}$ cm.$^{-2}$	10—11	448	420	11—12

Rearrangement of Amines.—In each case the amine was fused with the alkaline reagent in the absence of air, and volatile products were examined as well as the melt. Although the working-up differed in detail in the several cases, strongly and weakly basic, neutral, and acidic materials were in general separated; one experiment with dibenzylaniline (G) is described in detail as typical.

NN-Dibenzylaniline (5 g.) was fused with sodamide (6 g.) at 250—270° for 1·5 hr. under nitrogen. The melt was deep red, and a distillate collected in a receiver cooled in acetone–carbon dioxide. This was free from aniline (bleaching powder reaction) and benzaldehyde (dinitrophenylhydrazine), and gave on nitration 2,4-dinitrotoluene (mixed m. p.). The melt was dissolved in ether and dilute ethanol. Part of the ethereal layer, distilled *in vacuo*, gave a colourless oil which evidently contained benzylideneaniline since hydrolysis with hydrochloric acid gave aniline (recognised as benzeneazo-β-naphthol) and benzaldehyde (as dinitrophenylhydrazone). A second part was shaken with 7N-hydrochloric acid, but no precipitate was obtained, indicating the absence of 1,2,*N*-triphenylethylamine. The ether was removed and the residue steam-distilled, giving stilbene, rhombic prisms, m. p. 123° (from ethanol); with bromine in acetic acid it yielded plates of stilbene dibromide, m. p. 236°.

In a separate experiment, 1,2,*N*-triphenylethylamine [8] was fused with sodamide at 250° for 45 min. None was recovered, and stilbene (as dibromide) and aniline (as benzanilide) were recognised.

The synthesis of 9-benzyl-*N*-phenylfluorenylamine was attempted, unsuccessfully, in three ways. (*a*) 9-Benzylfluoren-9-ol was treated with hydrogen chloride in ether; the crude product reacted very slowly with aniline in ether. (*b*) *N*-Phenyl-9-fluorenylamine was converted into the *benzoyl derivative*, m. p. 147° (Found: C, 86·1; H, 5·3; N, 4·2. $C_{26}H_{19}ON$

[8] Busch and Rinck, *Ber.*, 1905, **38**, 1767.

requires C, 86·4; H, 5·3; N, 3·9%), which was treated with benzyl chloride and sodamide in liquid ammonia. (*c*) Fluorenone anil, added to benzylpotassium in toluene, and refluxed for 3 hr., gave only *N*-phenyl-9-fluorenylamine.

Synthesis of Phenanthrene.—6,7-Dihydro-6-phenyl-5*H*-dibenz[*c*,*e*]azepine [9] (IX) (1 g.) was heated with an excess of sodamide at 250° for 2 hr. A sublimate of phenanthrene was produced (m. p. and mixed m. p. 99°; m. p. and mixed m. p. of picrates, 144°), and aniline distilled. The residue afforded more phenanthrene (300 mg. in all) and aniline (benzoyl derivative, m. p. and mixed m. p. 160°).

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[9] Wenner, *J. Org. Chem.*, 1951, **16**, 1475.