668. *Molecular Rearrangement of Tertiary Amines. Part I.*

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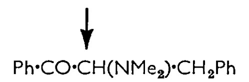
It is shown that under rather energetic alkaline conditions, certain tertiary amines of the type R·CO·CH_2·NArR′ rearrange to secondary amines, R·CO·CHR′·NHAr.

IT has been shown[1] that molecular rearrangement such as (i) is a fairly general reaction, depending on the acidity of the proton to be removed in the first stage and



$$\begin{array}{ll}[\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}NMe_2{\cdot}CH_2Ph}]^+\mathrm{OH}^- \rightleftharpoons \mathrm{Ph{\cdot}CO{\cdot}\overset{-}{C}H{\cdot}\overset{+}{N}Me_2{\cdot}CH_2Ph} & .\ .\ .\ .\ (i) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\downarrow & \\ \qquad\qquad\qquad\qquad\qquad\mathrm{Ph{\cdot}CO{\cdot}CH(NMe_2){\cdot}CH_2Ph} & \end{array}$$

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[1] Stevens *et al.*, *J.*, **1928**, 3193, and later papers.

on the nature of the migrating radical, usually benzyl or allyl in type. An analogous rearrangement of a tertiary amine, $R^1\cdot CH_2\cdot NR^2R^3 \xrightarrow{1} R^1\cdot\bar{C}H\cdot NR^2R^3 \xrightarrow{2} R^1\cdot CHR^3\cdot\bar{N}R^2 \xrightarrow{3} R^1\cdot CHR^3\cdot NHR^2$, would be expected to be less easy, first, because of the lower acidity of the proton to be extracted at stage 1, and secondly because the decisive stage 2 involves the passage of the nitrogen atom from the stable neutral tercovalent state to that of bicovalency with an anionic charge. In the case first chosen for study, the second disadvantage was mitigated by the attachment of a phenyl group to the nitrogen atom, and rearrangement of the compound (I) was in fact effected:

$$\text{(I)}\ Ph\cdot CO\cdot CH_2\cdot NPh\cdot CH_2Ph \longrightarrow Ph\cdot CO\cdot CH(NHPh)\cdot CH_2Ph\ \text{(II)}$$

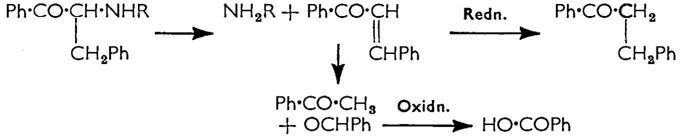
The product (II), of well-established constitution,[2] was obtained in a yield of over 40% by use of potassium hydroxide at 150°; it was accompanied by smaller amounts of benzoic acid, benzylaniline, aniline, and phenethyl phenyl ketone. Similar yields of compound (II) were obtained when the reaction was carried out in emulsion in diphenyl ether, with potassium hydroxide in less than an equivalent amount of phenol, or when the base (I) was fused with sodamide. The rearrangement could not be effected in a homogeneous medium so as to permit kinetic study: potassium hydroxide in ethylene glycol or in cyclohexanol, or sodium methoxide or sodium pentyl oxide in the corresponding alcohol gave benzylaniline in quantity, but not the amine (II). The use of acetaldehyde dibutyl acetal[3] as a solvent led to separation of potassium hydroxide and only a small yield of compound (II).

The effect of structural changes in the amine was investigated with the results shown in the Table. In cases B and C the small yield of rearranged base was accounted for, at least in part, by its limited stability under the conditions of reaction. Independent experiments suggest course (ii) for this decomposition. This scheme is supported by the isolation of benzoic acid in case F. It is perhaps not surprising that compound E, containing a nitro-group, gave only decomposition products; it appeared to be decomposed even by dilute aqueous alkali. The failure of an aryl group to migrate in case J conforms with

	Yield (mols. %) from compound *									
Product	A	B	C	D	E	F	G	H	I	J
R·CO·CHR′·NHAr	43	>3	10	30	—	60	10	10—15	—	—
R·CO·CH$_2$R′	2—5 [a]	17	5	—	—	—	—	~1 [b]	—	—
Ph·CO$_2$H	2—10 [c]	22 [c]	40 [c]	—	+ [c]	+ [c]	25	+	—	—
NHArR′	2 [d]	2—3 [c]	—	—	+ [c]	—	+	+ [b]	—	+ [e]
NH$_2$Ar	+	25 [g]	30—40 [h]	—	+ [i]	—	—	+ [j]	—	—
Temp.	150°	150°	150°	150°	140°	150°	100°	150°	100°	100°; 140°
Time (min.)	120	120	120	120	15	120	240	30	240	180 90

* A, $Ph\cdot CO\cdot CH_2\cdot NPh\cdot CH_2Ph$; B, $Ph\cdot CO\cdot CH_2\cdot N(C_6H_4\cdot OMe)\cdot CH_2Ph$; C, $Ph\cdot CO\cdot CH_2\cdot N(C_6H_4Ph)\cdot CH_2Ph$; D, $Ph\cdot CO\cdot CH_2\cdot NPh\cdot CH_2\cdot C_6H_4Ph$; E, $Ph\cdot CO\cdot CH_2\cdot NPh\cdot CH_2\cdot C_6H_4\cdot NO_2$; F, $CMe_3\cdot CO\cdot CH_2\cdot NPh\cdot CH_2Ph$; G, $Ph\cdot CO\cdot CH_2\cdot NPh\cdot CHMePh$; H, $Ph\cdot CO\cdot CH_2\cdot NPh\cdot CH_2\cdot CH{:}CH_2$; I, $Ph\cdot CO\cdot CH_2\cdot NPh\cdot CHPh_2$; J, $Ph\cdot CO\cdot CH_2\cdot NPh_2$.

Identification: [a] mixed m. p.; semicarbazone, m. p. 143°; [b] see experimental part; [c] mixed m. p.; [d] benzoyl derivative (mixed m. p.); hydrochloride, m. p. 198°; [e] m. p. 54°; [f] benzeneazo-β-naphthol (mixed m. p.); [g] mixed m. p.; methoxybenzeneazo-β-naphthol, m. p. 138°; [h] mixed m. p.; benzoyl derivative, m. p. 234°; [i] benzanilide (mixed m. p.); [j] purple colour with hypochlorite.



$$\begin{tikzcd} \underset{CH_2Ph}{Ph\cdot CO\cdot CH\cdot NHR} \arrow[r] & NH_2R + Ph\cdot CO\cdot CH{=}CHPh \arrow[r, "Redn."] \arrow[d] & \underset{CH_2Ph}{Ph\cdot CO\cdot CH_2} \\ & Ph\cdot CO\cdot CH_3 + OCHPh \arrow[r, "Oxidn."] & HO\cdot COPh \end{tikzcd}$$

. . . . (ii)

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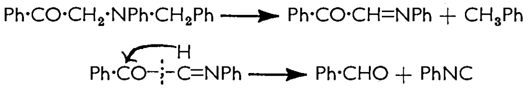
[2] McGeoch and Stevens, *J.*, 1935, 1032.

[3] Weizmann, Bergmann, and Sulzbacher, *J. Org. Chem.*, 1950, **15**, 918.

experience with quaternary ammonium compounds. Example I is based on a single experiment on difficulty accessible material.

In each experiment a strong smell of isocyanide was evident when the tertiary amine was ground with potassium hydroxide. Following Wedekind and Bruch,[4] who made similar observations, we formulate the change as:



$$Ph{\cdot}CO{\cdot}CH_2{\cdot}NPh{\cdot}CH_2Ph \longrightarrow Ph{\cdot}CO{\cdot}CH{=}NPh + CH_3Ph$$

$$Ph{\cdot}CO{-}\overset{H}{C}{=}NPh \longrightarrow Ph{\cdot}CHO + PhNC$$

The required tertiary amines were prepared by interaction of the appropriate bromo-ketone and secondary amine in presence of sodium hydrogen carbonate. The products of rearrangement (II and its analogues) were usually identified by synthesis from an arylamine and the related bromo-ketone, *e.g.*, $Ph{\cdot}CO{\cdot}CHBr{\cdot}CH_2Ph$.

An independent synthesis of the product in case F could not be effected. While hydrogenation of t-butyl styryl ketone was unselective, t-butyl phenethyl ketone was obtained by direct benzylation of t-butyl methyl ketone. Treatment of the bromo-derivative of this ketone gave in place of the expected $C_{19}H_{23}ON$ an anomalous product $C_{19}H_{25}ON$ whose infrared absorption showed the presence of anilino- and hydroxyl groups, but not of carbonyl. The product of rearrangement had the normal analysis and absorption, and on reduction gave aniline and t-butyl phenethyl ketone, so that its constitution is not in doubt.

Case G is complicated by possible diastereoisomerism in the product and in the precursor in its synthesis. The known 1-bromo-2-phenylpropyl phenyl ketone in reaction with aniline and sodium hydrogen carbonate gave much of an isomeric bromo-compound, believed to be the diastereoisomer produced by inversion at the carbon atom carrying bromine. The weakly basic material produced at the same time was oily and no doubt a mixture of stereoisomers; on submission to alkaline treatment approximating to that used in the rearrangement it yielded a substantial quantity of solid base identical with the rearrangement product; this solid appears to be the predominant form after alkali-promoted epimerisation of the mixed stereoisomerides.

In case H, owing to rapid spontaneous resinification, the products were hydrogenated at once, and the resulting 1-anilinobutyl phenyl ketone was identified by synthesis in the usual way. Here acetophenone was also formed as a by-product in the rearrangement.

EXPERIMENTAL

Ligroin had b. p. 60—80°.

Preparation of Secondary Bases.—*N*-Benzyl-*p*-anisidine was prepared (50%) by adding benzyl chloride (20 g.) to *p*-anisidine (25 g.) and sodium hydrogen carbonate (50 g.) in ethanol (60 ml.) with stirring at 50—60° and refluxing for 1 hr. It had b. p. 213—225°/20 mm., m. p. 50° after crystallisation from ligroin (lit.,[5] 52°). *N*-Benzyl-4-biphenylylamine, prepared in the same way, had m. p. 98° (Found: N, 5·4. Calc. for $C_{19}H_{17}N$: N, 5·4%) (with a by-product, presumably *NN*-dibenzyl-4-biphenylylamine). It was obtained almost quantitatively by catalytic reduction of benzylidene-4-biphenylylamine.[6]

40% Aqueous formaldehyde (100 ml.) and *p*-phenylbenzaldehyde [7] (182 g.) in methanol (700 ml.) were stirred during addition of sodium hydroxide (120 g.) in water (120 ml.) at 65—75°. After 40 min. at 75°, the mixture was boiled for 20 min. and diluted with water, the oil separated, and the aqueous layer extracted with ether. The oil and the ethereal extract were combined and dried, the ether removed, and the residue heated with phthalic anhydride (150 g.) at 115—120° for 1 hr. with stirring. The *hydrogen phthalate*, separated by means of sodium hydrogen carbonate, crystallised from benzene–ligroin in prisms, m. p. 121—123° (Found: C,

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[4] Wedekind and Bruch, *Annalen*, 1929, **471**, 83.
[5] Fröhlich and Wedekind, *Ber.*, 1907, **40**, 1010.
[6] Bell and Kenyon, *J.*, 1926, 2707; Bauer, Cymerman, and Sheldon, *J.*, 1951, 2344.
[7] Hey, *J.*, 1931, 2476.

75·6; H, 4·8. $C_{21}H_{16}O_4$ requires C, 75·9; H, 4·8%); refluxing for 30 min. with dilute alkali liberated 4-biphenylylmethanol, m. p. 98—100° (lit.,[8] 101—102°). The alcohol (2 g.) was refluxed with 50% hydrobromic acid (7·2 g.) for 2 hr. and the crude bicarbonate-washed and dried bromide was dissolved in benzene with aniline (4 ml.). After 18 hr. N-(*4-biphenylylmethyl*)*aniline* was separated through its hydrochloride (sparingly soluble in 8N-hydrochloric acid); crystallised from ethanol, it had m. p. 86—88° (Found: C, 87·3; H, 6·6; N, 5·8. $C_{19}H_{17}N$ requires C, 88·0; H, 6·6; H, 5·4%). The same base was prepared by hydrogenation of *N*-4-biphenylylmethyleneaniline in ethyl acetate, satisfactorily over palladium–charcoal but not over platinic oxide.

N-4-Nitrobenzylaniline [9] and *N*-α-methylbenzylaniline [10] were prepared by known methods; the latter crystallised from ethanol as needles, m. p. 27—28°. *N*-Allylaniline, prepared by adding allyl bromide (60 g.) during ½ hr. to aniline (200 ml.), sodium hydrogen carbonate (126 g.), and water (50 ml.) stirred on the steam-bath under reflux, boiled at 102—110°/15 mm. Busch and Rinck's method [11] for the preparation of *N*-diphenylmethylaniline was inferior in our hands to the reaction of benzylideneaniline with phenyl-lithium (1·33 mols.) in ether. After 1 hr. at reflux, the base was precipitated as hydrochloride, m. p. 199°, with 4N-hydrochloric acid. The distilled free base solidified slowly and crystallised, reluctantly, from ethanol in rectangular plates, m. p. 55—56°.

Preparation of Tertiary Bases.—Phenacyl bromide (1 mol.) and *N*-benzylaniline (2 mols.) were dissolved in benzene. After several days the solid benzylaniline hydrobromide was removed, and the benzene evaporated; the residue afforded thick, pale yellow needles, from ethanol, of N-*benzyl*-N-*phenacylaniline*, m. p. 107—108° (Found: C, 83·8; H, 6·4. $C_{21}H_{19}ON$ requires C, 83·7; H, 6·4%). Bauer and Bühler,[12] who obtained apparently the same compound in a similar manner, described it as 1-benzyl-3-phenylindole, $C_{21}H_{17}N$. It was produced in better yield [13] by refluxing phenacyl bromide (1 mol.) with *N*-benzylaniline (1 mol.) and sodium hydrogen carbonate (3 mols.) in ethanol for 3—4 hr. The filtered solution deposited benzylphenacylaniline (57%) in needles, m. p. 109°. These were interconvertible with the denser material of lower m. p. obtained by the other procedure, and the compound appears to be dimorphous. The pale yellow compounds listed in the annexed Table were prepared similarly, from phenacyl bromide, or in case F bromomethyl t-butyl ketone,[14] and a secondary base. In case I, the reactants were refluxed in benzene with sodium hydrogen carbonate for 60 hr.; the benzene layer was then shaken with 5N-hydrochloric acid, precipitating *N*-diphenylmethylaniline hydrochloride, and evaporated. The residue, crystallised from ethanol–ligroin, gave first " β-bromodiphenacyl," m. p. 160—161° (Found: C, 60·9; H, 4·2. Calc. for $C_{16}H_{13}O_2Br$: C, 60·6; H, 4·1%), and then *N*-diphenylmethyl-*N*-phenacylaniline. This preparation could not be repeated, nor could the required base be obtained by treating phenacyl bromide with diphenylmethylanilinomagnesium bromide or from diphenylmethyl bromide and phenacylaniline.

				Found (%)				Required (%)		
Case	Form	Solvent [a]	M. p.	C	H	N	Formula	C	H	N
B	Needles	Lig	98—99°	79·7	6·4	4·3	$C_{22}H_{21}O_2N$	79·7	6·4	4·2
C [b]	Prisms	EtOH	110—112	85·9	6·1	3·4	$C_{27}H_{23}ON$	85·9	6·1	3·7
D [c]	Plates	EtOH	126—128	85·5	6·1	3·7	$C_{27}H_{23}ON$	85·9	6·1	3·7
E	Plates	Lig	143	72·4	5·2	7·9	$C_{21}H_{18}O_3N_2$	72·8	5·2	8·1
F [b]	Octahedra [d]	Et_2O–Lig	97—99	81·1	8·2	4·7	$C_{19}H_{23}ON$	81·1	8·2	5·0
G [e]	Rhombs	Lig	127	83·6	6·5	—	$C_{22}H_{21}ON$	83·8	6·7	—
H [f]	Needles	EtOH	91	81·7	6·8	5·8	$C_{17}H_{17}ON$	81·3	6·8	5·6
I	Needles	EtOH–Lig	148—149	86·1	6·0	3·9	$C_{27}H_{23}ON$	85·9	6·1	3·7
J [g]	Flakes [h]	Lig	144	83·3	6·2	5·1	$C_{20}H_{17}ON$	83·6	5·9	4·9

[a] Lig = ligroin. [b] Components refluxed for 24 hr. [c] Components stirred at 67° for 24 hr. [d] Colourless. [e] Prepared in benzene. [f] Components stirred for 30 hr. at 60°. [g] From phenacyl bromide (1 mol.) and diphenylamine (2 mols.) in benzene without bicarbonate. [h] Orange-yellow.

Phenacyl bromide failed to react with *N*-triphenylmethylaniline or *N*-phenyl-9-fluorenylamine.

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[8] von Braun and Engel, *Annalen*, 1924, **436**, 306.
[9] Paal and Sprenger, *Ber.*, 1897, **30**, 69.
[10] Busch, *Ber.*, 1904, **37**, 2691.
[11] Busch and Rinck, *Ber.*, 1905, **38**, 1767.
[12] Bauer and Bühler, *Arch. Pharm.*, 1924, **262**, 128.
[13] Cf. Verkade and Janetzky, *Rec. Trav. chim.*, 1943, **62**, 775.
[14] Widman and Wahlberg, *Ber.*, 1911, **44**, 2066.

Rearrangement of Tertiary Bases.—In a typical experiment, *N*-benzyl-*N*-phenacylaniline (3 g.) was ground with potassium hydroxide (10 g.) and the mixture heated with stirring under nitrogen. The cooled melt was dissolved in water and ligroin. The separated aqueous layer gave benzoic acid on acidification. Agitation of the ligroin layer with 5N-hydrochloric acid precipitated a colourless hydrochloride (X); the acid aqueous filtrate afforded, on basification, oily *N*-benzylaniline and contained aniline. The residue from the evaporation of the ligroin layer was distilled in steam, giving phenethyl phenyl ketone. Basification of the hydrochloride (X) afforded α-anilinophenethyl phenyl ketone (II), identical (mixed m. p.) with an authentic specimen.[2] Considerable resinification took place, and the yield of ketone (II) depended on the time and temperature of the reaction:

Temp.	130°	145°	150°	150°	150°	170°
Time (hr.)	2	2	1	2	4	2
Yield (%)	27	37	30	43	27	25

A similar method was used in other cases. Neutral products were separated into steam-volatile and non-volatile fractions. Basic materials were extracted from ether or ligroin by dilute and by more concentrated hydrochloric acid, ketonic bases being manifestly weaker; and some secondary bases were separated as sparingly soluble hydrochlorides. In case B, much *p*-anisidine sublimed during the alkaline fusion.

Products of Rearrangement and their Synthesis.—*Case B.* The hydrochloride precipitated by 6N-acid gave a yellow oily base which crystallised when seeded with synthetic *α-*p*-anisidinophenethyl phenyl ketone* and was identified therewith by mixed m. p. The synthetic base was prepared by stirring α-bromophenethyl phenyl ketone [1] (5·78 g.) and *p*-anisidine (3·1 g.) in ethanol (30 ml.) with sodium hydrogen carbonate (5·04 g.) for 7 hr. and then refluxing the mixture for 1 hr. Ether was added, the solution washed with water and N-hydrochloric acid, and the residue from evaporation of the solvents crystallised from ethanol, as thin, pale yellow prisms, m. p. 86—87° (Found: C, 79·8; H, 6·3; N, 4·7. $C_{22}H_{21}O_2N$ requires C, 79·7; H, 6·4; N, 4·2%). Heated with potassium hydroxide (3 g.) for 1 hr. at 150° under nitrogen, the base (0·5 g.) gave, as well as some tar and unchanged material (30 mg.), *p*-anisidine (47 mg.), benzoic acid (105 mg.), and phenethyl phenyl ketone (15 mg.).

Case C. *α-4-Biphenylylaminophenethyl phenyl ketone*, precipitated as hydrochloride by 7N-hydrochloric acid, was identical with material synthesised in the same way as in case B. It crystallised from ethanol in pale yellow prisms, m. p. 138—140° (Found: C, 86·2; H, 6·1; N, 3·7. $C_{27}H_{23}ON$ requires C, 85·9; H, 6·1; N, 3·7%). With potassium hydroxide at 150° it decomposed like its analogue, giving 4-biphenylylamine, benzoic acid, and phenethyl phenyl ketone, and but little unchanged base.

Case D. The product, *1-anilino-2-4′-biphenylylethyl phenyl ketone* was identical (mixed m. p.) with material synthesised as follows. Acetophenone (2·6 g.) and *p*-phenylbenzaldehyde [7] (3·4 g.) were stirred in 30% ethanol (15 ml.) containing sodium hydroxide (1·5 g.) at 30° for 2·5 hr. After freezing, the pale yellow *2-4′-biphenylylvinyl phenyl ketone* was collected and after crystallisation from ethanol had m. p. 109—110° (Found: C, 88·6; H, 5·8. $C_{21}H_{16}O$ requires C, 88·7; H, 5·6%); the *2,4-dinitrophenylhydrazone* crystallised from ethanol–xylene in red needles, m. p. 216° (Found: C, 69·6; H, 4·3. $C_{27}H_{20}O_4N_4$ requires C, 69·8; H, 4·3%). Hydrogenation (1 mol.) of the unsaturated ketone in ethyl acetate over platinic oxide gave *2-4′-biphenylylethyl phenyl ketone*, needles (from ethanol), m. p. 68—70° (Found: C, 87·6; H, 6·5. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%). This ketone was treated with bromine (1 mol.) in carbon tetrachloride at room temperature; hydrogen bromide was removed in a stream of air, the solvent evaporated, and the residue crystallised from ethanol. *2-4′-Biphenylyl-1-bromoethyl phenyl ketone* had m. p. 109° (Found: C, 69·5; H, 4·9; Br, 21·1. $C_{21}H_{17}OBr$ requires C, 69·1; H, 4·7; Br, 21·9%). The bromo-ketone (0·5 g.), aniline (1·5 ml.), and sodium hydrogen carbonate (3 g.) in ethanol (10 ml.) were refluxed for 4 hr. and the product isolated as in case B, crystallising from ethanol in very pale yellow needles, m. p. 94—96° (Found: C, 86·4; H, 6·4; N, 3·9. $C_{27}H_{23}ON$ requires C, 86·0; H, 6·1; N, 3·7%).

Case F. *α-Anilinophenethyl t-butyl ketone* crystallised from ligroin in needles, m. p. 123—124° (Found: C, 81·1; H, 8·1; N, 4·8. $C_{19}H_{23}ON$ requires C, 81·2; H, 8·2; N, 5·0%). This product was heated under reflux with 3N-sulphuric acid and zinc dust, the solid slowly disappearing. Ether extracted phenethyl t-butyl ketone, b. p. 140°/20 mm., recognised as oxime, and the acid solution contained aniline identified as benzeneazo-β-naphthol.

In attempts to synthesise the product of rearrangement, phenethyl t-butyl ketone was prepared (*a*) by hydrogenation of styryl t-butyl ketone [15] and (*b*) by benzylation of methyl t-butyl ketone in presence of sodamide.[16] The product of method (*a*) had b. p. 262°; unless more than 1·5 mols. of hydrogen had been absorbed, it was unsaturated towards permanganate and appeared to undergo addition as well as substitution with bromine, but it gave the known oxime, m. p. 96—97° (Found: C, 75·8; H, 9·3; N, 6·8. Calc. for $C_{13}H_{19}NO$: C, 76·1; H, 9·3; N, 6·8%). Method (*b*) gave a saturated product, b. p. 245°, which (3·8 g.) was treated with bromine (3·2 g.) in cold carbon tetrachloride (80 ml.); it could also be brominated by *N*-bromosuccinimide in boiling carbon tetrachloride. The crude bromo-compound, freed from solvent under reduced pressure, was stirred for 12 hr. with aniline (2·5 ml.) and sodium hydrogen carbonate (5 g.) in ethanol (30 ml.) and the whole was then refluxed for 1 hr. The small quantity of *substance* soluble in 2N-hydrochloric acid crystallised from ligroin in needles, m. p. 148—149° (Found: C, 80·3; H, 8·9; N, 4·7. $C_{19}H_{25}ON$ requires C, 80·1; H, 8·8; N, 4·9%). It was not affected by fusion with potassium hydroxide under the conditions of the rearrangement. Infrared maxima were at 1309 (anilino) and at 1265 and 1076 cm.$^{-1}$ (CH·OH), with no carbonyl band; the product of rearrangement absorbed at 1309 and at 1702 cm.$^{-1}$ (C=O).

Case G. The weaker bases were crystallised fractionally from ligroin, giving first yellow-green needles, m. p. 120°, of 1-*anilino*-2-*phenylpropyl phenyl ketone* (Found: C, 84·0; H, 6·4; N, 4·5. $C_{22}H_{21}ON$ requires C, 83·8; H, 6·7; N, 4·4%); later fractions consisted of unstable buff crystals which could not be purified.

Phenyl 2-phenylpropyl ketone was prepared in excellent yield by refluxing acetophenone with hydriodic acid and red phosphorus for 15 hr.[17] The derived bromo-compound [18] (9·1 g.) with aniline (3 g.) and sodium hydrogen carbonate (5 g.) in propan-1-ol were stirred and refluxed for 45 hr. The filtered solution deposited, on freezing, crystals of a diastereoisomeric 1-*bromo*-2-*phenylpropyl ketone*, m. p. 122° (from ethanol) (Found: C, 63·5, 63·7; H, 5·1, 5·3. $C_{16}H_{15}OBr$ requires C, 63·4; H, 5·0%). The mother-liquor was diluted and the separated yellow oil dissolved in ether, extracted with N-hydrochloric acid to remove aniline, and shaken with 5N-acid, giving a crystalline precipitate. The oily base (1 g.) recovered from this hydrochloride was heated with powdered potassium hydroxide in nitrogen at 100° for 2 hr. The base, recovered through its insoluble hydrochloride, then crystallised from ligroin at 0°, had m. p. 122—123·5°, and did not depress the m. p. of the product of rearrangement.

Case H. *N*-Allyl-*N*-phenacylaniline (1·3 g.) was fused with potasium hydroxide (3 g.) at 150° for ½ hr. The melt was taken up in ether and water, the dried ethereal solution evaporated, and the residue, which resinified on normal working-up, was hydrogenated in ethyl acetate over platinum oxide (uptake, 105 ml.). The aqueous layer afforded benzoic acid. The products of hydrogenation, dissolved in ether, were shaken, first with N-hydrochloric acid giving extract (X), then with 7N-acid, giving a red solution (Y) and a white solid (Z). After evaporation of the separated ether layer, the residue was distilled in steam and the volatile oil converted into mixed 2,4-dinitrophenylhydrazones. These, dissolved in chloroform, were chromatographed on Whatman No. 1 paper by ascent. Separately, but in the same apparatus at the same time, the dinitrophenylhydrazones of acetophenone and butyl phenyl ketone were similarly treated; the liquid phase was ether–ligroin (1 : 19 by volume). The R_F values for the separate dinitrophenylhydrazones were 0·02 and 0·89 respectively, and the solution under test gave two spots with these values. The remainder of the chloroform solution was adsorbed on alumina and eluted with ether–ligroin (1 : 19); the widely separated bands gave respectively butyl phenyl ketone dinitrophenylhydrazone (20 mg.; from ethanol–xylene) and acetophenone dinitrophenylhydrazone (from ethanol), which were identified with authentic specimens.

The extract (X) gave a transient purple colour with bleaching powder, and afforded *N*-propylaniline oxlate. Solution (Y) gave on basification a little N-*phenacyl*-N-*propylaniline*, identical with a specimen prepared by hydrogenating *N*-allyl-*N*-phenacylaniline over palladium black in ethanol: it formed pale yellow crystals (from ethanol), m. p. 96° (Found: C, 80·8; H, 7·5; N, 5·5. $C_{17}H_{19}ON$ requires C, 80·6; H, 7·5; N, 5·5%). The solid (Z) yielded an oily base which on benzoylation gave 1-*N*-benzoylanilinobutyl phenyl ketone, identical with material

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[15] Hill, Spear, and Lachowicz, *J. Amer. Chem. Soc.*, 1923, **45**, 1560.
[16] Hill and Bruce, *J. Amer. Chem. Soc.*, 1930, **52**, 348.
[17] Graebe, *Ber.*, 1874, **7**, 1625.
[18] Stevens, *J.*, 1930, 2114.

synthesised as follows. Butyl phenyl ketone (1·6 g.) was treated with bromine (1·6 g.) in cold carbon tetrachloride, hydrogen bromide removed in a stream of air, and the solvent evaporated. The residue was stirred at 50° for 20 hr. with aniline (1 ml.) and sodium hydrogen carbonate (2·5 g.) in ethanol (10 ml.). Ether was added, and the mixture shaken successively with water, N-hydrochloric acid, and 8N-acid; the last precipitated the hydrochloride of a base which was liberated and distilled, giving 1-*anilinobutyl phenyl ketone*, b. p. 120°/0·4 mm. (Found: C, 80·6; H, 7·5; N, 5·5. $C_{17}H_{19}ON$ requires C, 80·6; H, 7·5; N, 5·5%). The *benzoyl derivative* (Schotten–Baumann) melted at 86° (Found: C, 81·1; H, 6·4; N, 3·8. $C_{24}H_{23}O_2N$ requires C, 80·7; H, 6·4; N, 3·9%).

We thank the Carnegie Trustees for a Research Scholarship (to W. F. C.) and the University of Sheffield for an Ellison Fellowship (to R. A. W. J.).

THE UNIVERSITIES OF GLASGOW AND SHEFFIELD. [*Received, December* 30*th*, 1959.]