

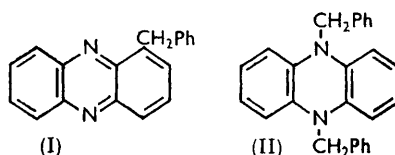
421. The Reaction of Phenazine with Free Benzyl Radicals.

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Benzyl radicals react easily with phenazine, giving 1-benzylphenazine and 5:10-dibenzyl-5:10-dihydrophenazine in the approximate ratio 3:1. C-Substituted di- and possibly tetra-benzylphenazines are also formed.

WORK in this laboratory has shown that benzyl radicals add to the *meso*-positions of anthracene¹ and acridine;² in the latter case the initial attack occurred at the carbon and not at the nitrogen centre, an inference corroborated by investigation of the 1:2- and 3:4-benzacridine.³ It was therefore of interest to investigate the benzylation of phenazine in which nitrogen occupies both *meso*-positions.

Phenazine proved very reactive since only about 1% of dibenzyl was formed by combination of benzyl radicals. The reaction yielded 1-benzylphenazine (I) and 5:10-dibenzyl-5:10-dihydrophenazine (II) in the approximate molar ratio of 3:1 and smaller amount of more highly C-substituted phenazines, but no trace of 2-benzylphenazine



was discovered. For reference, authentic 1- and 2-benzylphenazine were synthesised by oxidising 1- and 2-methylphenazine^{4,5} to the corresponding aldehydes, condensing these with phenylmagnesium bromide, oxidising the resulting alcohols to the benzoylphenazines, and reducing the latter by the Huang-Minlon method. 5:10-Dibenzyl-5:10-dihydrophenazine was prepared by benzylating the sodium adduct of phenazine.⁶

The theoretical implications of this study are two-fold. First, it gives clear evidence of some direct attack of hydrocarbon radicals on the nitrogen atoms of heterocyclic aromatic ring-systems, a feature of homolytic substitution that has not been established with pyridine or quinoline and was thought not to occur with acridine,² though the possibility of attack by benzoylperoxy-radicals on the nitrogen of pyridine and quinoline has recently been considered.⁷ Secondly, it shows that phenazine is much more reactive in the side rings than anthracene or acridine, combined with which is its marked tendency to form C-substitution rather than addition products and thus preserve the aromatic character of the whole molecule. Substitution in α - rather than in β -positions naturally accords with qualitative theoretical expectations.

EXPERIMENTAL

M. p.s are corrected.

Phenazine was prepared from 2-nitrodiphenylamine in 60% yield by Waterman and Vivian's method.⁸

Reactions with Benzyl Radicals.—(i) Phenazine (5 g.) and *tert.*-butyl peroxide (8.2 g., 2 mol.) were refluxed under nitrogen in dry toluene (400 ml.) for 7 days. After removal of solvent the residual black gum (9.4 g.) was taken up in light petroleum-benzene (9:1) and chromatographed

¹ Beckwith and Waters, *J.*, 1957, 1001.

² Waters and Watson, *J.*, 1957, 253.

³ Waters and Watson, preceding paper.

⁴ McCombie, Scarborough, and Waters, *J.*, 1928, 353.

⁵ Vivian, Hartwell, and Waterman, *J. Org. Chem.*, 1954, **19**, 1641.

⁶ Mikhailov and Blokhina, *Izvest. Acad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1950, 304; *Chem. Abs.*, 1950, **44**, 9452.

⁷ Pausacker, *Austral. J. Chem.*, 1958, **11**, 200.

⁸ Waterman and Vivian, *J. Org. Chem.*, 1949, **14**, 289.

through alumina (300 g.). It yielded green-grey needles (260 mg.) which after sublimation at 200°/0.5 mm. and crystallisation from light petroleum gave yellow needles of 5 : 10-dibenzyl-5 : 10-dihydrophenazine, m. p. and mixed m. p. (see below) 213—214.5° (Found: C, 86.6; H, 6.3; N, 7.5. $C_{26}H_{22}N_2$ requires C, 86.2; H, 6.1; N, 7.7%). Further elution with benzene gave mixtures of phenazine and benzylphenazines. From further similar experiments, this mixture was separated by steam-distillation into a trace of dibenzyl (<2%), volatile phenazine, m. p. and mixed m. p. 173—174°, and involatile 1-benzylphenazine, yellow needles (from light petroleum), m. p. and mixed m. p. (see below) 120—121° (Found: C, 84.0; H, 5.1; N, 10.4. $C_{19}H_{14}N_2$ requires C, 84.4; H, 5.2; N, 10.4%), which was oxidised by chromium trioxide in acetic acid to 1-benzoylphenazine, yellow needles (from methanol), m. p. and mixed m. p. 196—197° (Found: C, 80.1; H, 4.3; N, 10.2. $C_{19}H_{12}ON_2$ requires C, 80.2; H, 4.3; N, 9.9%). There were also isolated from the involatile material a dibenzylphenazine (2.5%) crystallising in yellow needles, m. p. 171—173° (Found: C, 86.7; H, 5.7; N, 7.5. $C_{26}H_{20}N_2$ requires C, 86.7; H, 5.6; N, 7.8%), and a smaller amount of a tetrabenzylphenazine, as yellow needles, m. p. 198—200° (Found: C, 88.8 ± 0.4; H, 6.0 ± 0.7; N, 4.7 ± 0.5 in 5 analyses. $C_{40}H_{32}N_2$ requires C, 88.8; H, 6.0; N, 5.2%).

(ii) Phenazine (10 g.) and *tert.*-butyl peroxide (8 g., 0.9 mol.) were refluxed under a stream of pure nitrogen in dry toluene (500 ml.) for 76 hr. Steam-distillation of the resulting material separated 5.8 g. (58%) of phenazine and by chromatography there were obtained 1 g. (5%) of 5 : 10-dibenzyl-5 : 10-dihydrophenazine, 2.5 g. (16.5%) of 1-benzylphenazine, and traces of yellow polybenzylphenazines with m. p.s in the range 205—220°. None of the infrared spectra of these fractions had a band at 814 cm^{-1} indicative of 2-benzylphenazine.

The dibenzylphenazine of m. p. 171—173° is not 1 : 4-dibenzylphenazine, which is known;⁹ it may well be 1 : 5-dibenzylphenazine.

Preparation of Reference Compounds.—1-Methylphenazine, m. p. 107—108° (lit., 108°), was obtained in 37% yield by heating 2-methyl-2'-nitrodiphenylamine⁴ with 10 times its weight of degreased iron filings (cf. ref. 8) and then oxidised with freshly sublimed selenium dioxide to 1-formylphenazine, m. p. 176—177° (lit.,^{10,11} 175°), by Rozum's method.¹⁰ To this aldehyde (2 g.) in tetrahydrofuran (200 ml.) was added, under nitrogen, a filtered solution of phenylmagnesium bromide (from 6 g. of bromobenzene) in ether. After completion of the reaction the product, 1- α -hydroxybenzylphenazine (1.4 g.), was purified chromatographically and crystallised from methanol in fine yellow needles, m. p. 126—127° (Found: C, 79.8; H, 4.8; N, 9.9. $C_{19}H_{14}ON_2$ requires C, 79.7; H, 4.9; N, 9.8%). This alcohol (0.3 g.) was oxidised at 100° with chromium trioxide (0.1 g.) in acetic acid (4 ml.) to 1-benzoylphenazine (0.18 g.) which crystallised from methanol in stout yellow needles, m. p. 196—197° (Found: C, 80.4; H, 4.6; N, 9.6%). This material (0.18 g.) was reduced with 100% hydrazine hydrate (2 ml.) and potassium hydroxide (1.5 g.) in diethylene glycol (10 ml.) and gave 1-benzylphenazine (0.15 g.) as yellow needles [from light petroleum (b. p. 40—60°)], m. p. 121—122° (Found: C, 84.7; H, 5.1; N, 10.1%).

Phenazine	$\lambda_{max.}$ (Å)	log ϵ	$\lambda_{max.}$ (Å)	log ϵ	Phenazine	$\lambda_{max.}$ (Å)	log ϵ	$\lambda_{max.}$ (Å)	log ϵ
1-Methyl ...	2515	5.2	3630	4.2	Dibenzyl (m. p. 171—173°)	2565	5.0	3650	4.2
2-Methyl ...	2515	5.2	3645	4.2	Tetrabenzylphenazine				
1-Benzyl ...	2520	5.1	3635	4.2	(m. p. 199—200°)	2670	—	3730	—
1-Benzoyl ...	2490	5.0	3645	4.2	5 : 10-Dibenzyl-5 : 10-di-	2500	4.9	2530*	4.8
2-Benzyl ...	2565	5.0	3650	4.2	hydro	3530	4.0	3590*	4.0

* In chloroform.

From 2-methylphenazine, m. p. 117—118° (lit.,⁴ 117°), prepared similarly from 4-methyl-2'-nitrodiphenylamine, was obtained 2-formylphenazine, m. p. 187° (corr.) (lit.,¹⁰ 185°), and thence 2- α -hydroxybenzylphenazine which crystallised from methanol in yellow plates, m. p. 174—174.5° (Found: C, 79.8; H, 5.0; N, 9.6%). Oxidation of this, as described above, gave 2-benzoylphenazine, yellow needles (from methanol), m. p. 130—131° (Found: C, 70.8; H, 4.2; N, 9.6%), from which by Huang-Minlon reduction was obtained 2-benzylphenazine, yellow needles (from light petroleum), m. p. 106—107.5° (Found: C, 84.7; H, 5.3; N, 10.1%).

⁹ McIlwain, J., 1937, 1701.

¹⁰ Rozum, *Zhur. obshchei Khim.*, 1955, 25, 611.

¹¹ Birkofer and Birkofer, *Chem. Ber.*, 1952, 85, 286.

5 : 10-Dibenzyl-5 : 10-dihydrophenazine was prepared by adding sodium chips (1.8 g.) to a stirred suspension of phenazine (1.75 g.) in liquid ammonia (300 ml.); after 45 min. the deep blue colour was discharged by addition of benzyl chloride, ammonia was allowed to evaporate from the resulting yellow solution, and the remainder after treatment with water was steam-distilled. From the residue (2.3 g.) the dibenzyl-dihydrophenazine crystallised on addition of benzene and had m. p. and mixed m. p. 213—214.5° with material obtained from the reaction described above. The same substance was obtained in 44% yield by shaking phenazine (1.1 g.), sodium (0.4 g.), and glass chips in 1 : 2-dimethoxyethane (20 ml.) under nitrogen for 36 hr.⁶ and then decomposing the sodium adduct with benzyl chloride; this had m. p. 213—214.5° (Found: C, 86.3; H, 6.2; N, 7.7%).

Ultraviolet Spectra of Phenazine Derivatives in Ethanol.—These are reported in the Table.

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