

### 359. *The Reaction of Tertiary Benzyl-amines with Free tert.-Butoxy-radicals.*

By R. L. HUANG.

Tertiary benzyl-amines  $\text{Ph}\cdot\text{CH}_2\cdot\text{NRR}'$  are dehydrogenated by free *tert.*-butoxy-radicals to the radicals  $\cdot\text{CHPh}\cdot\text{NRR}'$  which then dimerise and disproportionate, to extents depending on the nature of R and R'.

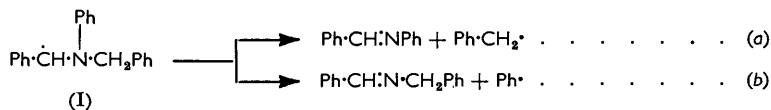
THE reaction of *tert.*-butoxy-radicals with benzyl ethers  $\text{Ph}\cdot\text{CH}_2\cdot\text{OR}$  proceeds<sup>1</sup> by abstraction of hydrogen to generate radicals  $\cdot\text{CHPh}\cdot\text{OR}$ , which then disproportionate into benzaldehyde and the free radical R $\cdot$ , or dimerise, or both, depending on the nature of R. The reaction of the same radicals with tertiary benzyl-amines  $\text{Ph}\cdot\text{CH}_2\cdot\text{NRR}'$ , containing a system analogous to that in benzyl ethers, is now reported.

With *tert.*-butyl peroxide as the source of radicals as before, the following benzylamines have been studied: tribenzylamine, dibenzylaniline, dibenzylethylamine, benzylethylaniline, benzyldiphenylamine, and benzyldiethylamine (see Table for a summary of results). Although in general reaction appears to be more complex than with benzyl ethers, the products isolated, which consist of the dimer (II), accompanied in some cases by the anil (III), are best explained as derived from the intermediate aminobenzyl radical  $\cdot\text{CHPh}\cdot\text{NRR}'$ , analogous to that formed from benzyl ethers, by dimerisation and disproportionation to  $\text{Ph}\cdot\text{CH}\cdot\text{NR} + \text{R}'$ .

Compared with benzyl ethers the amines, in particular those with alkyl substituents, afford more polymers. These could result from the anils produced, or from unstable enamines such as obtained from tertiary alkylamines and benzoyl peroxide.<sup>2</sup> As evidence for the first possibility it has been found that benzyldeneaniline polymerises under the reaction conditions more readily than benzaldehyde, and that, in experiments with tribenzylamine and dibenzylaniline, the yields of anils dropped sharply when a higher molar ratio (1 : 1) of the peroxide was used.

The aminobenzyl radicals also display a somewhat greater tendency towards dimerisation, a process characteristic of more stable radicals. In general, presence of an NPh group favours dimerisation, and enhances the yield of isolable products, whereas progressive substitution by ethyl rapidly increases the complexity of the products.

As with the alkoxybenzyl radicals, the behaviour of the radical  $\cdot\text{CHPh}\cdot\text{NRR}'$  depends on the nature of the substituents. Thus disproportionation of the radical (I) could take course (a) or (b), of which the former is preferred, since the latter would involve generation of the highly energetic phenyl radical.

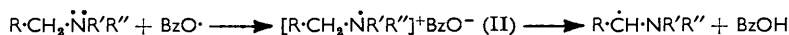


<sup>1</sup> Huang and Si-Hoe, *Proc. Chem. Soc.*, 1957, 354; *idem* in "Vistas in Free Radical Chemistry," ed. W. A. Waters, Pergamon Press, London, in the press.

<sup>2</sup> Buckley, Dunstan, and Henbest, *J.*, 1957, 4880, 4901.

For the same reason, the radical  $\cdot\text{CHPh}\cdot\text{NPh}_2$  does not disproportionate, but only dimerises.

For reaction of amines with benzoyl peroxide Horner and his co-workers<sup>3</sup> suggest participation of radical intermediates, although Buckley *et al.* prefer an ionic mechanism.<sup>2</sup> Horner<sup>3a</sup> visualises the initial formation of an aminium radical-ion (II) which on loss of a proton gives rise to an aminoalkyl radical, as follows:



If such a radical-ion were first formed, the removal of an  $\alpha$ -hydrogen atom as proton in the next step would, in the case of a nuclear-substituted dibenzylamine, depend on the polar nature of the substituent. This does not appear to be supported by recent findings<sup>3b</sup> with monosubstituted dibenzylanilines. With *tert.*-butoxy-radicals we consider that tertiary benzyl-amines undergo dehydrogenation in a manner analogous to that of the benzyl ethers,<sup>1</sup> alkylbenzenes, acids, etc.,<sup>4</sup> and that the reaction does not involve the hetero-atom in the system. However, an attempt to substantiate this by subjecting *N*-benzyl-*N*-*p*-nitrobenzylaniline to reaction with *tert.*-butyl peroxide gave inconclusive results.

*Products from reaction of tertiary benzyl-amines with tert.-butyl peroxide.<sup>a</sup>*

Amine		Products (yield, %)		Amine		Products (yield, %)	
Ph·CH <sub>2</sub> ·NRR'		Anil	Dimer	Ph·CH <sub>2</sub> ·NRR'		Anil	Dimer
R	R'	Ph·CH·NR	[Ph·CH·NRR'] <sub>2</sub>	R	R'	Ph·CH·NR	[Ph·CH·NRR'] <sub>2</sub>
Ph	Ph	—	40 <sup>b</sup>	Ph·CH <sub>2</sub>	Ph·CH <sub>2</sub>	32	4
Ph	Ph·CH <sub>2</sub>	27	37	"	"	Trace	0 <sup>c</sup>
"	"	Trace	24 <sup>bc</sup>	"	"	35	0 <sup>d</sup>
Ph	Et	0	33	Ph·CH <sub>2</sub>	Et	0	18
				Et	Et	0	0

<sup>a</sup> A 3—4 molar excess of the amine was used, the reaction being carried out in a sealed tube. The yield was calculated on the amine which reacted. <sup>b</sup> Both *meso* and racemic forms isolated. <sup>c</sup> A 1 : 1 molar ratio of amine and peroxide was used. <sup>d</sup> In an open flask under nitrogen.

### EXPERIMENTAL

*Tribenzylamine.*—(a) The amine (14.6 g.; m. p. 93°) and *tert.*-butyl peroxide (2.5 g.) were sealed under nitrogen and heated at 100° for 2 days and at 110° for 2 more days. The mixture was extracted with boiling methanol, the solid (0.25 g.) which survived extraction being  $\alpha$ -*bis*dibenzylaminodibenzyl, m. p. 252—254° (from benzene) (Found: C, 88.4; H, 7.1; N, 5.0. C<sub>42</sub>H<sub>40</sub>N<sub>2</sub> requires C, 88.1; H, 7.0; N, 4.9%). The methanolic extract, when chilled, deposited unchanged tribenzylamine (4.4 g.; m. p. and mixed m. p.) which was filtered off. The filtrate was concentrated, filtered from a small crop of the above dibenzyl (0.05 g.), then distilled to give the following fractions: (i) material, b. p. 130—140°/0.5 mm. (1.5 g.),  $n_D^{24}$  1.5919; (ii) tribenzylamine, b. p. ca. 160°/0.5 mm. (3.4 g.), m. p. and mixed m. p. 93°; and (iii) a brown residue (2.9 g.). Fraction (i) was mostly *N*-benzylidenebenzylamine (32%, calc. on amine which reacted). It gave an immediate precipitate of benzaldehyde 2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p.) with Brady's reagent, and on further distillation had b. p. 118—122°/0.5 mm.,  $n_D^{24}$  1.5931 (lit.,<sup>5</sup>  $n_D^{17.5}$  1.6011) (Found: C, 86.1; H, 6.9; N, 6.8. Calc. for C<sub>14</sub>H<sub>13</sub>N: C, 86.1; H, 6.7; N, 7.1%). A portion (0.4 g.) was hydrogenated in ethanol over Raney nickel, 40 c.c. of hydrogen being absorbed in 30 min., to give dibenzylamine, b. p. 130° (bath)/0.3 mm. 0.24 g.,  $n_D^{22}$  1.5730 (lit.,  $n_D^{22}$  1.5743), which formed a benzoyl derivative, m. p. and mixed m. p. 113—115°.

(b) With a 1 : 1 molar ratio of amine and peroxide, only unchanged amine and polymer, and traces of the anil (as detected by Brady's reagent), were obtained.

(c) The reactants were heated under reflux in an atmosphere of nitrogen at 110° for 4 days, to give unchanged amine (70%) and *N*-benzylidenebenzylamine (35%), no dimer being encountered.

<sup>3</sup> (a) Horner, *Angew. Chem.*, 1950, **62**, 359; (b) Horner and Kirmse, *Annalen*, 1955, **597**, 48, and earlier papers.

<sup>4</sup> *E.g.*, Farmer and Moore, *J.*, 1951, 131; Huang and Morsingh, *J.*, 1953, 160; Huang and Kum Tatt, *J.*, 1954, 2570; 1955, 4229.

<sup>5</sup> Mignouac, *Ann. Chim. (France)*, 1934, **2**, 225.

*Dibenzylaniline.*—(a) The amine (13.2 g., m. p. 67°) and *tert.*-butyl peroxide (1.8 g.) were sealed and heated as before, and the resulting mixture was extracted with boiling methanol. The solid which remained was racemic  $\alpha\beta$ -bisbenzylphenylaminodibenzyl, m. p. ca. 210° (1.8 g., 37%) raised to 223—225° by recrystallisation from benzene-ethanol from which it separated in stout rods (Found: C, 88.3; H, 6.65.  $C_{40}H_{36}N_2$  requires C, 88.2; H, 6.7%). The methanolic extract, after decantation from a brown viscous oil (0.5 g.), gradually deposited unchanged amine (6.8 g.) which was collected. The filtrate was concentrated and distilled, giving volatile material and the following fractions: (i) Benzylideneaniline, b. p. 106—112°/0.5 mm. (0.85 g., 27%) (an authentic sample had b. p. 104—106°/0.2 mm.); (ii) unchanged amine, b. p. 152—161°/0.5 mm. (1.6 g.), m. p. and mixed m. p. 67°; and (iii) a small residue (ca. 0.5 g.). Fraction (i) crystallised when seeded with benzylideneaniline, and after recrystallisation from aqueous ethanol had m. p. 45°, alone or mixed with an authentic sample (m. p. 52°). Further recrystallisation, however, did not raise the m. p. A portion (0.42 g.), hydrogenated in ethanol over Raney nickel, absorbed 42 c.c. of hydrogen in 2.5 hr. to give benzylaniline, identified as the benzoyl derivative (ca. 0.2 g.), m. p. 104—105°, alone or with an authentic sample of m. p. 107°.

(b) The amine (7.0 g., 0.026 mole) and the peroxide (3.8 g., 0.026 mole), heated as above, gave racemic  $\alpha\beta$ -bisbenzylphenylaminodibenzyl (1.13 g.) and the *meso-isomer*, which was relatively insoluble in benzene, and crystallised from ethyl acetate in rectangular prisms, m. p. 242—245° (0.27 g.) (Found: C, 88.3; H, 6.6; N, 6.7%) (total yield of dimers, 24%). The methanolic extract afforded no crystalline material, and on chromatography (light petroleum on alumina) followed by distillation gave only small quantities of unchanged amine (0.6 g.) and intractable oils. No benzylideneaniline was isolated, although its presence could be detected by means of Brady's reagent, with which it formed benzaldehyde 2 : 4-dinitrophenylhydrazone.

(c) Heating the reaction mixture at 90—100° for 4 days resulted in a 84% recovery of the amine, and a 19% yield of the racemic dimer.

Benzylideneaniline (20 g.) and the peroxide (4.0 g.) after the usual treatment gave unchanged anil (12 g.) and a tar, chromatography of which afforded only intractable oils.

*Dibenzylethylamine.*—The amine (15.0 g.,  $n_D^{22}$  1.5562) and *tert.*-butyl peroxide (2.5 g.), after being heated as above, were distilled through a 6-cm. Vigreux column, to give volatile material, unchanged amine (8.4 g.; b. p. 100—101°/0.05 mm.,  $n_D^{22}$  1.5578), and a viscous residue (4.0 g.), but no *N*-benzylidene-ethylamine. The residue, on chromatography on alumina in light petroleum, gave the fractions: (i) material (1.4 g.) which on evaporative distillation gave unchanged amine (0.50 g.) and  $\alpha\beta$ -bis(benzylethylamino)dibenzyl, b. p. 170—190° (bath)/0.05 mm. (0.54 g.), which crystallised in contact with ethanol and had m. p. 121—130°, raised to 127.5—130° after further crystallisations from ethanol-benzene (Found: C, 85.6; H, 7.9; N, 6.3.  $C_{32}H_{36}N_2$  requires C, 85.7; H, 8.1; N, 6.2%); (ii) an oil (0.8 g.) which on distillation gave more unchanged amine (0.13 g.), the dibenzyl above (0.55 g.), and a small residue; (iii) small fractions of intractable liquids.

*N-Benzyl-N-ethylaniline.*—The amine (19.0 g.;  $n_D^{24}$  1.5937) and the peroxide (3.4 g.) were heated at 110—115° for two days. Fractionation with a 10-cm. Vigreux column then gave volatile material, unchanged peroxide (0.7 g.), unchanged amine (14.3 g.), and a viscous residue, there being no intermediate fraction between the unused peroxide and amine. The residue, adsorbed on alumina and eluted with petroleum, gave fractions: (i) yellow liquid (1.3 g.) which on distillation afforded more unchanged amine (0.55 g.) and a residue which in contact with methanol deposited  $\alpha\beta$ -bis(ethylanilino)dibenzyl, needles (from methanol), m. p. 124° (0.31 g.) (Found: C, 85.9; H, 7.5; N, 6.4.  $C_{30}H_{32}N_2$  requires C, 85.7; H, 7.6; N, 6.7%); (ii) the same dibenzyl (1.1 g.); and four further fractions of oil.

*Benzylidiphenylamine.*—The amine (12.5 g.; m. p. 89—90°) and the peroxide (3.6 g.) were heated at 125—131° for 25 hr. The mixture soon darkened and, after ca. 4 hours' heating, crystals separated. The almost black reaction mixture was extracted with boiling ethanol (ca. 80 c.c.), and the solid which remained was recrystallised from benzene to give *meso*- $\alpha\beta$ -bisdiphenylaminodibenzyl, prisms decomp. ~264°, m. p. 281° (0.29 g.) (Found: C, 88.6; H, 6.4; N, 5.3.  $C_{38}H_{32}N_2$  requires C, 88.4; H, 6.2; N, 5.4%). The ethanol extract, on cooling, yielded (i) a sticky green solid (ca. 1.5 g. of impure starting material), (ii) crystals A (9.9 g.), and (iii) more unchanged amine (0.2 g.). Solid A was mainly unchanged amine, and on treatment with boiling ethanol (25 c.c.) mostly dissolved, leaving racemic  $\alpha\beta$ -bisdiphenylaminodibenzyl, which was soluble in benzene but only slightly so in ethanol, and crystallised from a mixture of these

solvents in stout rods, m. p. 222—223° (0.1 g.) (Found: C, 88.4, 88.5; H, 6.4, 6.2%). A solution of the *meso*-isomer in chloroform slowly became dark green.

*Benzyl-diethylamine and N-Benzyl-N-p-nitrobenzylaniline.*—Only unchanged amine and intractable oils were obtained after similar reactions with these bases.

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UNIVERSITY OF MALAYA, SINGAPORE.

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