Homosolvolysis. Part 3.[1] The Reaction of Aromatic Acid Chlorides with Di-t-butyl Nitroxide

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N-Aroyl-*O*-aroyl-*N*-t-butylhydroxylamines are formed when aromatic acid chlorides react with di-t-butyl nitroxide.

Previous parts have shown that reactive carbon–halogen bonds can undergo homosolvolysis when treated with persistent radicals such as nitroxides,[2] *e.g.* reaction (1). The new radical

$$RX + (Me_3C)_2NO^\bullet \longrightarrow R^\bullet + Me_3\overset{+}{N}{=}O\ Cl^- \quad (1)$$

can react further with unchanged nitroxide to yield products formed either (2a) by radical combination or (2b) by atom transfer.

$$R^\bullet + (Me_3C)_2NO^\bullet \begin{cases} \xrightarrow{a} (Me_3C)_2NOR \\ \xrightarrow{b} RH + Me_3CNO + Me_2C{=}CH_2 \end{cases} \quad (2)$$

In particular benzoyl chloride was reported to react with di-t-butyl nitroxide to yield the benzoyl radical [reaction (3)].[2] The benzoyl radical can react with further nitroxide to

$$PhCOCl + (Me_3C)_2NO^\bullet \longrightarrow PhCO^\bullet + (Me_3C)_2\overset{+}{N}O\ Cl^- \quad (3)$$

yield *O*-benzoyl-*NN*-di-t-butylhydroxylamine [reaction (4)].[2]

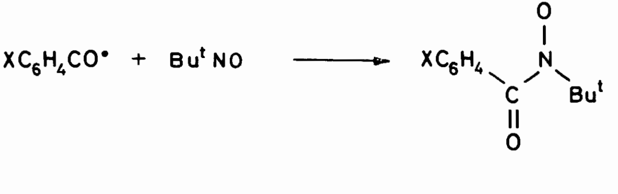
$$PhCO^\bullet + (Me_3C)_2NO^\bullet \longrightarrow PhCO_2N(Me_3C)_2 \quad (4)$$

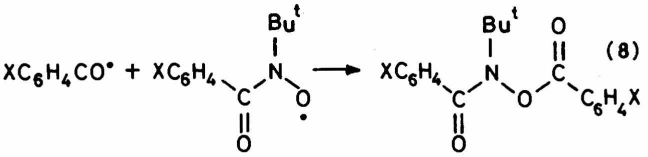
We have confirmed this observation but in the experimental conditions reported in this paper a less soluble product, *N*-benzoyl-*O*-benzoyl-*N*-t-butylhydroxylamine, was obtained. The yield was low but the compound was easy to isolate because of its relative insolubility. The reaction was extended to seven other aroyl chlorides. The first step is the homosolvolysis of the aroyl chloride (XC_6H_4COCl) to yield the aroyl radical and the nitroxide chloride [reaction (5)].

$$XC_6H_4COCl + (Me_3C)_2NO^\bullet \longrightarrow XC_6H_4CO^\bullet + (Me_3C)_2\overset{+}{N}{=}O\ Cl^- \quad (5)$$

The aroyl radical formed in (5) reacts with further nitroxide to yield the benzaldehyde (XC_6H_4CHO), 1,1-dimethylnitrosoethane, and 2-methylpropene [reaction (6)]. Further aroyl radicals combine with the dimethylnitrosoethane to give a radical addition product [reaction (7)]. The final step involves combination with a third aroyl radical to yield *N*-aroyl-*O*-aroyl-*N*-t-butylhydroxylamine. The experiment was completed with eight different acid chlorides (*i.e.* XC_6H_4COCl, X = H; *p*-Me; *o*-Me; *p*-MeO; Cl; *p*-Me_3C; CF_3; and 2-furoyl).

$$XC_6H_4CO^\bullet + (Me_3C)_2NO^\bullet \longrightarrow XC_6H_4CHO + Me_3CNO + Me_2C{=}CH_2 \quad (6)$$


(7)


(8)

Although the yields of purified product are very low, the *N*-aroyl-*O*-aroyl-*N*-t-butylhydroxylamines are relatively insoluble and hence can be isolated from a complex mixture.

It was not possible to isolate the intermediate benzaldehyde (or substituted benzaldehyde) from the reaction mixtures, but it was possible to establish its presence. Degassed benzoyl chloride and di-t-butyl nitroxide were sealed in an n.m.r. tube. After 24 h the n.m.r. spectrum due to the nitroxide had disappeared and a singlet (δ 10.20) characteristic of an aldehyde appeared. The spectrum underwent no further change when the sample was retained for a week.

Toluene-4-sulphonyl chloride was treated with di-t-butyl nitroxide in dry benzene. The reaction proceeded and the volatile products, 2-methylpropene and 1,1-dimethylnitrosoethane, were formed as before, but no product analogous to the *N*-aroyl-*O*-aroyl-*N*-t-butylhydroxylamine could be isolated. Phenacyl bromide in benzene was treated with the di-t-butyl nitroxide but no visible reaction occurred.

Experimental

N.m.r. spectra were recorded with a Bruker ER 200 D spectrometer, and m.p.s. were determined using an AEI 902 instrument.

The aroyl chloride was added to di-t-butyl nitroxide and a steady stream of nitrogen was passed through the mixture. As the reaction proceeded the red nitroxide changed to green, and finally the solution became blue. The volatile products were collected in a cold trap (solid CO_2) and were shown to be 2-methylprop-1-ene and 1,1-dimethyl-1-nitrosoethane. The reaction was continued until the blue colour disappeared to leave a solid which was taken up in ether leaving an insoluble residue, which was identified as impure nitroxide chloride [*e.g.* for reaction with PhCOCl (Found: C, 52.7; H, 9.9; N, 7.1. Calc. for $C_8H_{18}ClNO$: C, 53.4; H, 10.1; N, 7.8%)]. The ether solution was evaporated and the mixture was pumped to remove any unchanged acid chloride. The crude product from benzoyl chloride (1.07 g) was crystallised from light petroleum (b.p. 40—60 °C) to give *N*-benzoyl-*O*-benzoyl-*N*-t-butylhydroxylamine (0.10 g), m.p. 84—85 °C; δ($CDCl_3$) 8.81—8.88 (m) and 1.60 (s) (Found: *m/z*, 297.1354; C, 72.8; H, 6.65; N, 4.7. $C_{18}H_{19}NO_3$ requires *m/z*, 297.1365; C, 72.7; H, 6.4; N, 4.7%).

4-Toluoyl chloride (1.18 g) was treated with di-t-butyl nitroxide (2.0 g) to give purified N-*t-butyl*-N-*4′-toluoyl*-O-*4″-toluoylhydroxylamine* (0.17 g), m.p. 110—111 °C; δ($CDCl_3$) 7.40 (4 H, dd, *J* 22.0 and 9.0 Hz), 7.20 (4 H, dd, *J* 18.0 and 9.0 Hz), 2.35 (3 H, s), 2.20 (3 H, s), and 1.55 (9 H, s) (Found: *m*/*z*, 325.1664; C, 73.6; H, 7.2; N, 4.3. $C_{20}H_{23}NO_3$ requires *m*/*z*, 325.1678; C, 73.8; H, 7.1; N, 4.3%).

4-Anisoyl chloride (1.30 g) was treated with di-t-butyl nitroxide (2.0 g) and gave purified N-*4′-anisoyl*-O-*4″-anisoyl*-N-*t-butylhydroxylamine* (0.10 g), m.p. 84—85 °C; δ($CDCl_3$) 7.24 (4 H, dd, *J* 40.0 and 9.0 Hz), 7.15 (4 H, dd, *J* 35.0 and 9.0 Hz), 3.85 (3 H, s), 3.73 (3 H, s), and 1.58 (9 H, s) (Found: *m*/*z*, 357.1554; C, 67.00; H, 6.9; N, 3.9. $C_{20}H_{23}NO_5$ requires *m*/*z*, 357.1576; C, 67.0; H, 6.75; N, 3.9%).

4-Chlorobenzoyl chloride (1.34 g) was treated with di-t-butyl nitroxide (2.0 g) and gave purified N-*4′-chlorobenzoyl*-O-*4″-chlorobenzoyl*-N-*t-butylhydroxylamine* (0.18 g), m.p. 87—88 °C; δ($CDCl_3$) 7.55 (4 H, dd, *J* 16.0 and 9.0 Hz), 7.33 (4 H, dd, *J* 11.0 and 9.0 Hz), and 1.55 (9 H, s) (Found: *m*/*z*, 365.0550; C, 59.05; H, 4.7; N, 3.8. $C_{18}H_{17}ClNO_3$ requires *m*/*z*, 365.0585; C, 59.0; H, 4.7; N, 3.8%).

4-t-Butylbenzoyl chloride (1.50 g) was treated with di-t-butyl nitroxide (2.0 g) and gave purified N-*t-butyl*-N-*4′-butylbenzoyl*-O-4″-butylbenzoylhydroxylamine (0.18 g), m.p. 118—119 °C; δ($CDCl_3$) 7.53 (4 H, dd, *J* 17.0 and 9.0 Hz), 7.30 (4 H, dd, *J* 12.5 and 9.0 Hz), 1.55 (9 H, s), 1.28 (9 H, s), and 1.15 (9 H, s) (Found: *m*/*z*, 409.2640; C, 76.0; H, 8.7; N, 3.4. $C_{26}H_{35}NO_3$ requires *m*/*z*, 409.2617; C, 76.25; H, 8.6; N, 3.4%).

4-Trifluoromethylbenzoyl chloride (1.58 g) was treated with di-t-butyl nitroxide (2.0 g) which gave purified N-*t-butyl*- N-*4′-trifluoromethylbenzoyl*-O-*4″-trifluoromethylbenzoylhydroxylamine* (0.19 g), m.p. 145—146 °C; δ_H($CDCl_3$) 8.78 (4 H, dd, *J* 32.0 and 8.8 Hz), 8.63 (4 H, dd, *J* 14.0 and 6.4 Hz), and 1.63 (9 H, s); δ_F 63.645 and 64.066 p.p.m. (Found: *m*/*z*, 433.1092. $C_{20}H_{17}F_6NO_3$ requires *m*/*z*, 433.1092).

2-Toluoyl chloride (1.18 g) was treated with di-t-butyl nitroxide (2.0 g) which gave purified N-*t-butyl*-N-*2′-toluoyl*-O-*2″-toluoylhydroxylamine* (0.17 g), m.p. 60—61 °C; δ($CDCl_3$) 7.23 (8 H, complex), 2.40 (3 H, s), 2.30 (3 H, s), and 1.63 (9 H, s) (Found: *m*/*z*, 325.1670; C, 73.65; H, 7.2; N, 4.3. $C_{20}H_{23}NO_3$ requires *m*/*z*, 325.1679; C, 73.8; H, 7.1; N, 4.3%).

2-Furoyl chloride (0.90 g) was treated with di-t-butyl nitroxide (2.0 g) which gave purified N-*2′-furoyl*-O-*2″-furoyl*-N-*t-butylhydroxylamine* (0.19 g), m.p. 86—88 °C; δ($CHCl_3$) 7.71 (dd, *J* 1.6 and 0.8 Hz), 7.38 (dd, *J* 3.2 and 1.6 Hz), 7.02 (dd, *J* 3.4 and 0.8 Hz), 6.62 (dd, *J* 3.2 and 1.6 Hz), and 6.36 (dd, *J* 3.2 and 1.6 Hz) (Found: *m*/*z*, 277.0950; C, 60.5; H, 5.5; N, 5.0. $C_{14}H_{15}NO_5$ requires *m*/*z*, 277.0953; C, 60.6; H, 5.45; N, 5.05%).

Acknowledgements

We record wise counsel and advice received from Dr. J. C. Walton.

References

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Received 6*th October* 1986; *Paper* 6/1957