

Acyl Nitroxides. Part 2.¹ Reactions with Hydrocarbons

By S. Altaf Hussain, Terence C. Jenkins, M. John Perkins,* and Nancy P. Y. Siew, Department of Chemistry, Chelsea College, London SW3 6LX

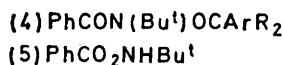
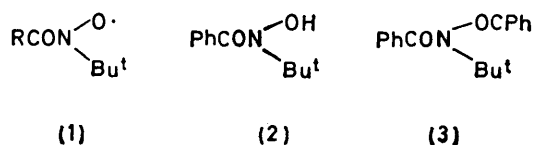
The reactions of benzoyl *t*-butyl nitroxide with a range of hydrocarbon substrates are described. Hydrogen abstraction (leading to substitution) is observed with alkenes having reactive allylic hydrogens, and with aralkanes. Other alkenes give addition products. With alkanes a radical self-reaction competes with hydrogen abstraction, although good yields of substitution product may sometimes be obtained using the more reactive 3,5-dinitrobenzoyl *t*-butyl nitroxide.

Kinetic data are reported for reaction of the benzoyl nitroxide with cumene [equation (3)], and relative reactivity data are recorded for other alkylbenzenes; using a series of substituted toluenes, correlation with σ^+ gives a ρ -value of -0.9 (at 90°C).

Reaction of the benzoyl nitroxide with a series of aldehydes gives *O*-acyl-*N*-benzoyl-*N*-*t*-butylhydroxylamines.

In Part 1 of this series¹ was described the synthesis of a number of readily isolated acyl *t*-butyl nitroxides (1). In this and forthcoming papers, we shall describe the reactions of these radicals, and shall discuss their spectroscopic properties and structure.

These stable acyl nitroxides are differentiated from the better known dialkyl nitroxides² by the strengths of the bonds which they form to hydrogen.³ Thus the OH bond strength in *N*-*t*-butylbenzohydroxamic acid (2) is *ca.* 322 kJ mol⁻¹, which is to be compared with a figure of *ca.* 300 kJ mol⁻¹ for unhindered *NN*-dialkylhydroxylamines.⁴ The magnitude of this difference is enhanced if the benzohydroxamic acid is substituted with an electron-withdrawing group, and this has led to the preparation of 3,5-dinitrobenzoyl *t*-butyl nitroxide [1; R = 3,5-(O₂N)₂C₆H₃] as a potentially useful oxidising agent.^{1,5} These radicals are, however, less reactive than the more extensively investigated bistrifluoromethyl nitroxide.⁶



In an unreactive solvent, such as benzene, benzoyl *t*-butyl nitroxide slowly decomposes to give the *NO*-diacylhydroxylamine (3) and 2-methyl-2-nitrosopropane. This self-reaction, which is a very slow first-order process in dilute solution, even at 80°C , will be considered in a subsequent paper. The present paper explores the reactivity of the benzoyl nitroxide towards a variety of hydrocarbons and related substrates. Since some of these reactions are quite slow, the substrate has usually been employed in large excess (frequently as solvent) to minimise incursion of the radical self-reaction. However, towards the end of the paper it is pointed out that more reactive substrates can frequently react in high

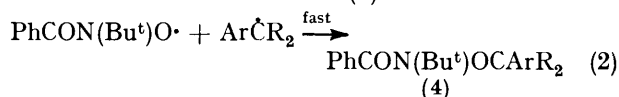
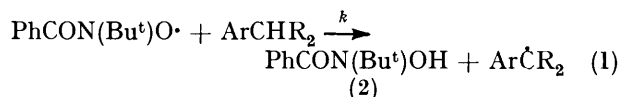
† Some of the results presented here were outlined in a preliminary form in ref. 5.

yield using correct molar ratios of radical and substrate in a suitably unreactive solvent.

It is pertinent to note that synthetic reactions with stable radicals have the attraction that the substrate-derived radical will be efficiently scavenged by the reservoir of stable radical, giving remarkably clean reactions. This is particularly so when the initial radical-substrate reaction is highly selective. Examples include the oxidation of phenols with Fremy's radical (the Teuber reaction⁷) and dehydrogenations using DPPH.⁸

RESULTS AND DISCUSSION †

The initial investigations were of the reactions of benzoyl *t*-butyl nitroxide with aralkanes. With aralkane as solvent, the reactions are quite clean according to equations (1) and (2), although it has been noted that the benzohydroxamic acid (2) may slowly rearrange into the *O*-benzoyl-derivative [(5), PhCO₂NHBu^t].‡



As expected from equations (1) and (2), the disappearance of nitroxide is cleanly first order; for cumene, the kinetic results obtained by following the reaction by e.s.r. fitted equation (3):

$$\begin{array}{l}
 k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = \\
 10^{(7.93 \pm 0.56)} \cdot \exp[-(74.9 \pm 3.8 \text{ kJ mol}^{-1})/RT] \quad (3)
 \end{array}$$

which has been adjusted to express the second-order rate constant (k) for equation (1). The activation energy of $74.9 \pm 3.8 \text{ kJ mol}^{-1}$ seems reasonable, and is close to the value of 70.3 kJ mol^{-1} determined for a similar oxidation employing di-*t*-butyliminoxyl which forms bonds to hydrogen of similar strength to those in (2).¹⁰

Reactions with toluene and ethylbenzene were studied in less detail, except that relative reactivities (at 75°C)

‡ This rearrangement, which is similar to those reported for other hydroxamic acids,⁹ will be discussed in a subsequent paper.

TABLE 1

Relative reactivities (per hydrogen) of alkanes towards hydrogen abstraction by free radicals

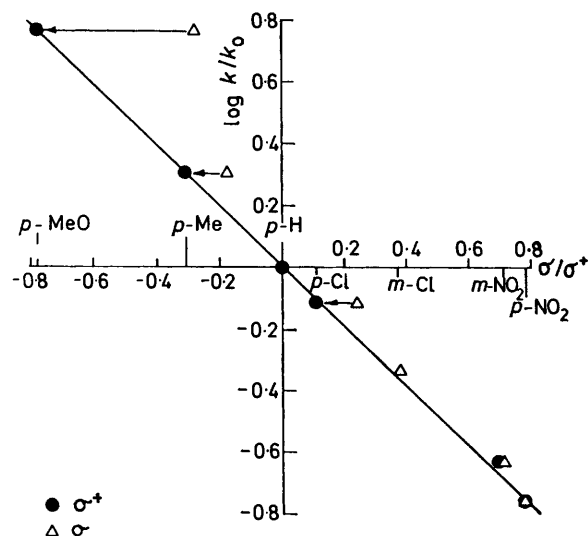
Radical R· (t/°C)	R-H Bond dissociation energy/kJ mol ⁻¹	Substrate			Ref.
		PhCH ₃	PhCH ₂ CH ₃	PhCH(CH ₃) ₂	
PhCON(Bu ^t)O· (75)	318	1	22	70	This work
PhCON(Bu ^t)O· (75)	318	1	32		This work
<i>p</i> -MeOC ₆ H ₄ CON(Bu ^t)O· (15)	326	1	38.5		This work
<i>p</i> -O ₂ NC ₆ H ₄ CON(Bu ^t)O· (15)	335	1	25		This work
Bu ^t OO· (30)	377	1	8.3	13	<i>a</i>
Cl ₃ C· (40)	402	1	50	260	<i>b</i>
(Bu ^t) ₂ C=NO· (120)	339	1	10	46	10
Br· (77)	364	1	25	57	<i>c</i>

^a E. F. Caldin, *Chem. Rev.*, 1969, **69**, 135. ^b G. A. Russell and C. DeBoer, *J. Amer. Chem. Soc.*, 1963, **85**, 3136. ^c S. S. Friedrich, E. C. Friedrich, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, 1969, **34**, 900.

were determined. Direct comparison of toluene and ethylbenzene was also carried out in a competition experiment in which the product yields were compared by n.m.r. The relative reactivities (per hydrogen) are compared in Table 1 with those for a variety of other radicals, including two substituted aryl nitroxides. For the latter the variation in selectivity is as expected in the light of the variation in OH bond strength in the corresponding hydroxamic acids.³ It is also noteworthy that the reactivity of the benzoyl nitroxide towards cumene is somewhat lower than might be expected by comparison with the selectivity of the other radicals listed. It is possible that this reflects the steric requirement of the bulky substituents on the nitroxide.

Several substituted toluenes were also compared with ethylbenzene in order to probe the sensitivity of the hydrogen abstraction to polar substituent effects. The results (Table 2; Figure) correlate well with σ^+ ($\rho =$

solution, hydrogen abstraction from a saturated compound (*e.g.* cyclohexane) did not compete very successfully with the self-reaction of the nitroxide, a yield of *ca.* 30% substitution product being the highest achieved. 2,3-Dimethylbutane also reacts rather inefficiently despite the presence of the tertiary hydrogens; some spectroscopic evidence was obtained for olefin formation and subsequent reaction of the allylic hydrogens of the product. However, in dilute solution in cyclohexane,



Hammett plot for hydrogen abstraction from substituted toluenes by benzoyl t-butyl nitroxide at *ca.* 90 °C (σ and σ^+ values from J. Shorter, 'Correlation Analysis in Organic Chemistry, and Introduction to Linear Free Energy Relationships,' Oxford University Press, 1974, and H. B. Amin and R. Taylor, *Tetrahedron Letters*, 1978, 267.

TABLE 2
Relative reactivities of substituted toluenes X·C₆H₄CH₃ towards benzoyl t-butyl nitroxide *

X·C ₆ H ₄ CH ₃	[ArCH ₃] : [PhEt]	Relative reactivity [k _{ArCH₃} /k _{PhEt}] (per benzylic hydrogen)
H	1 : 1	7.6 × 10 ⁻²
H	1 : 1.5	7.5 × 10 ⁻²
H	1 : 6	7.6 × 10 ⁻²
4-CH ₃	1 : 1	15.6 × 10 ⁻²
3-Cl	1 : 5	3.57 × 10 ⁻²
4-Cl	1 : 10	5.9 × 10 ⁻²
4-OCH ₃	1 : 1	44.4 × 10 ⁻²
3-NO ₂	1 : 10	1.78 × 10 ⁻²
4-NO ₂	1 : 15	1.36 × 10 ⁻²

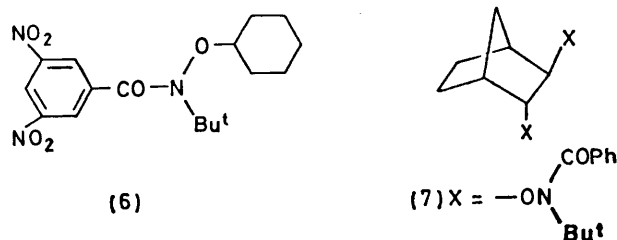
* Reactions at *ca.* 90 °C (see Experimental section).

-0.9 at *ca.* 90 °C), consistent with some electrophilic character in the nitroxide.*

The *O*-aralkylhydroxamates (4) formed in the above reactions all showed temperature-dependent n.m.r. spectra in the range -50 to +50 °C. In each case a conformational change with ΔG^\ddagger of *ca.* 54-59 kJ mol⁻¹ was indicated. A full investigation of this behaviour will be described in a separate paper.

Extension of the hydrogen-abstraction experiments to aliphatic hydrocarbons showed that, even in dilute

the more reactive t-butyl 3,5-dinitrobenzoyl nitroxide does give a good yield (*ca.* 70%) of substitution product (6). When this reaction was carried out in the presence

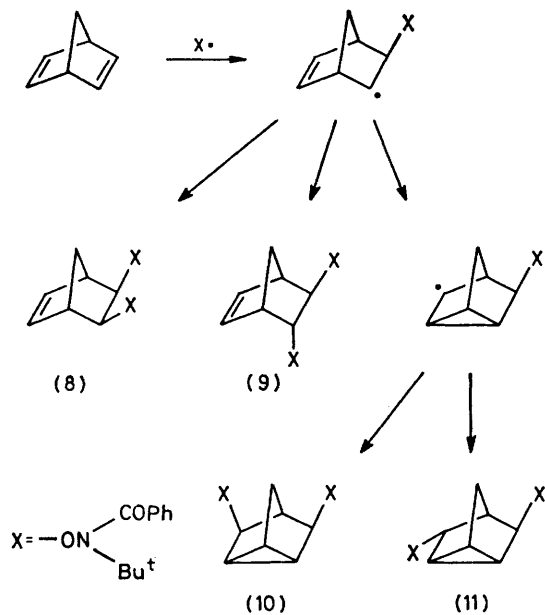


* For a recent discussion of polar effects in radical reactions see ref. 11.

of a ten-fold excess of iodine, cyclohexyl iodide was obtained in comparable yield.

Allylic abstraction, mentioned above, occurred readily. Thus with an excess of cyclohexene the allylic substitution was essentially quantitative, no addition product being detected. Addition does, however, occur with olefins having no reactive allylic hydrogens. Thus styrene gives a 2 : 1 adduct essentially quantitatively.

Norbornene gives predominantly the *trans*-adduct (7), while norbornadiene gives both normal and rearranged adducts (see Scheme); the presence of quite high concentrations of stable radical in the latter case was clearly insufficient to impede the rapid rearrangement of the intermediate norbornenyl radical. The products of both reactions were consistent with initial *exo*-attack

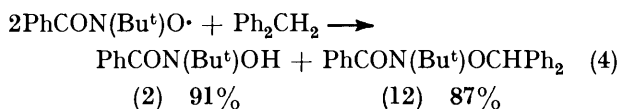


SCHEME

of radical on olefin as normally observed, although they do not demand this as the exclusive mode of reaction.¹²

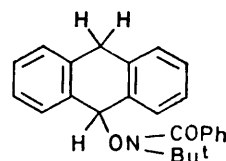
Experiments with both stilbene isomers gave a single isolated product, and whilst α -methylstyrene gives exclusive addition, β -methylstyrene was the only olefin examined for which substitution appears to occur competitively with addition.

Full comparison of the rates of reaction of the nitroxide with the wide variety of hydrogen donor substrates has not been undertaken. However, as noted at the outset, many substrates were sufficiently reactive for the radical self-reaction to be ignored. This is exemplified by the reaction in benzene of two equivalents of nitroxide with one of diphenylmethane, which leads to (2) and (12) in excellent yield [reaction (4)].



Interestingly, further reaction of the product seems unimportant, probably as a consequence both of the bulk of the nitroxide, and of steric inhibition of resonance in the substituted benzhydryl radical which would be formed.

Cyclohexadiene is cleanly oxidised to benzene by the benzoyl nitroxide, but 9,10-dihydroanthracene reacts in diethyl ether with two equivalents of the radical to give predominantly the substitution product (13)

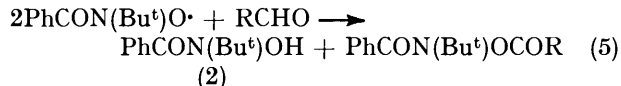


(13)

(91%) and only a trace of anthracene. This contrasts with the recently reported oxidation of dihydroanthracene by diphenyl nitroxide.¹³

Aldehydes were also oxidised by two equivalents of nitroxide, affording *O*-acyl-*N*-benzoyl-*N*-*t*-butylhydroxylamines in yields usually in excess of 80% [reaction (5)].

Qualitatively it was noted that the reactivities of substituted benzaldehydes varied in the same fashion as did those of substituted toluenes, consistent with the electrophilic character of the nitroxide.



EXPERIMENTAL

Routine procedures and instrumentation were as detailed in Part 1.¹ Cumene and ethylbenzene were distilled under N_2 and other substrates were purified by distillation or crystallisation before use. Chemical-ionisation mass spectrometry used isobutane in a Micromass spectrometer.

Reactions of Benzoyl t-Butyl Nitroxide with Aromatic Compounds.—(i) *Toluene.* A solution of the nitroxide (348 mg) in a mixture of benzene (45 cm³) and toluene (17.3 g) was boiled under reflux until the colour of the nitroxide was discharged (ca. 2 h). The solution was cooled, the bulk of the solvent was removed *in vacuo*, and the remainder by chromatography of the residue on a column of silica which was eluted with hexane. The reaction products were then eluted with diethyl ether, solvent was removed, and the residual oil was separated by preparative t.l.c. on silica gel (CH_2Cl_2) to give *N*-*t*-butylbenzohydroxamic acid (2) (90 mg, 72% after crystallisation from light petroleum), and a less polar oil (195 mg, ca. 100%) having spectroscopic properties consistent with its identification as *O*-benzoyl *N*-*t*-butylbenzohydroxamate [ν_{max} (CCl_4) 1 650 cm⁻¹; δ (35 °C, CDCl_3) 1.60 (s, 9 H, Bu^t), 4.48 (s, 2 H, CH_2), and 6.5–7.7 (m, 10 H, 2 × Ph); m/e 284 ($M^+ + 1$) (Chemical ionisation)]. It was later shown that this product may have been contaminated with *O*-benzoyl-*N*-*t*-butylhydroxylamine.

(ii) *Substituted toluenes.* Essentially the same procedure was adopted as that described above for toluene, except that the hydroxamic acid was extracted from the reaction mix-

ture ($3 \times 30 \text{ cm}^3$ 2M-NaOH) prior to solvent removal. Products obtained were as follows. From *p*-methoxytoluene, *O-p-methoxybenzyl N-t-butylbenzohydroxamate*, m.p. 65.5°C [62% from hexane; ν_{max} (Nujol) 1650 cm^{-1} ; $\delta(35^\circ\text{C}, \text{CCl}_4)$ 1.5 (s, 9 H, Bu^t), 3.75 (s, 3 H, OCH₃), 4.43 (s, 2 H, CH₂), and 6.6–7.9 (m, 9 H, aromatic) (Found: C, 72.9; H, 7.65; N, 4.2%. C₁₉H₂₃NO₃ requires C, 72.8; H, 7.3; N, 4.5%). From *p*-xylene, *O-p-methylbenzyl N-t-butylbenzohydroxamate*, m.p. 110°C [65% from hexane; ν_{max} (Nujol) 1651 cm^{-1} ; $\delta(35^\circ\text{C}, \text{CCl}_4)$ 1.58 (s, 9 H, Bu^t), 2.27 (s, 3 H, CH₃), 4.42 (s, 2 H, CH₂), and 6.52–7.78 (m, 9 H, aromatic) (Found: C, 76.7; H, 7.9; N, 4.6%. C₁₉H₂₃NO₂ requires C, 76.8; H, 7.7; N, 4.7%). From *p*-chlorotoluene, *O-p-chlorobenzyl N-t-butylbenzohydroxamate*. This crystallised as needles, m.p. 62°C , from hexane–CCl₄, but the crystals contained CCl₄, which was slowly lost. After powdering, and drying *in vacuo* for 18 h, a sample had an analysis consistent with that for the solvent-free material [Found: C, 67.9; H, 6.3; Cl, 11.51; N, 4.4%. C₁₈H₂₀ClNO₂ requires C, 68.0; H, 6.3; Cl, 11.2; N, 4.4%]. The spectra were very similar to those of related compounds. From *m*-chlorotoluene, *O-m-chlorobenzyl N-t-butylbenzohydroxamate* was obtained as a colourless oil with spectra similar to those of related compounds [*m/e* 318 (*M*⁺ + 1)]. With *p*-nitrotoluene a yellow low-melting (*ca.* 30°C) solid, and with *m*-nitrotoluene a yellow oil were obtained, both in *ca.* 70% yield, being respectively *O-p-nitrobenzyl* and *O-m-nitrobenzyl N-t-butylbenzohydroxamate*. The spectra of these compounds were as expected; neither was further purified.

(iii) *Cumene and ethylbenzene*. Following essentially the procedure employed for the substituted toluenes, cumene gave *O-(α,α -dimethylbenzyl) N-t-butylbenzohydroxamate* as a colourless oil [89%; ν_{max} (CCl₄) 1647 cm^{-1} ; $\delta(25^\circ\text{C}, \text{CDCl}_3)$ 1.28 (s, 9 H, Bu^t), 1.39 (broad s, 6 H, CMe₂), and 7.1–7.7 (m, 10 H, 2 Ph); *m/e* 312 (*M*⁺ + 1)]; similarly, ethylbenzene gave *O-(α -methylbenzyl) N-t-butylbenzohydroxamate* as a colourless oil [83%; ν_{max} (CCl₄) 1640 cm^{-1} ; $\delta(35^\circ\text{C}, \text{CDCl}_3)$ 1.18 (d, *J* 6.7 Hz, 3 H, CH₃), 1.45 (s, 9 H, Bu^t), 4.58 (q, *J* 6.7 Hz, 1 H, CH), and 6.75–7.55 (m, 10 H, 2 Ph); *m/e* 298 (*M*⁺ + 1)].

(iv) *Competition experiments*. Separate solutions of benzoyl *t*-butyl nitroxide (*ca.* 250 mg) in a mixture of ethylbenzene and a toluene of known molar composition (*ca.* 10 cm³/total) and benzene (*ca.* 10 cm³) were deoxygenated (N₂) and then refluxed under N₂ until decolourised. The hydroxamic acid was removed by base washing, and the bulk solvent was removed by filtration through a column of silica gel. The products were then eluted with diethyl ether, and examined by n.m.r., carefully integrating the CH quartet in the product from ethylbenzene, and the CH₂ singlet in the product from the toluene. The results are collected in Table 1. The reaction with a (benzene-free) mixture of toluene and ethylbenzene was also conducted at room temperature (*ca.* 15°C , N₂), and was repeated using the *p*-nitro- and *p*-methoxy-derivatives of the benzoyl nitroxide. The results are given in Table 1.

(v) *Kinetics experiments*. Cumene was further purified by repeated washing with concentrated H₂SO₄ until the washings were colourless, with aqueous NaHCO₃, and with water, and dried (MgSO₄). It was then distilled under N₂ prior to use from Ph₃P–MgSO₄ to remove any traces of hydroperoxide. Solutions of nitroxide in cumene (*ca.* 10⁻⁴M) were prepared and each was equilibrated (N₂) for a few minutes in the cavity of the Varian E4 e.s.r. spectrometer at the working temperature to be employed. The

decay of a single spectral line was then monitored. Acceptable experiments gave linear first-order plots for at least 3 half-lives after measurement commenced. The first-order rate constants were corrected for the cumene concentration at that temperature (neat *ca.* 7M) to give second-order rate constants represented by equation (3), which was obtained from the results of experiments at nine different temperatures in the range 60–90°C. Temperatures were determined with a calibrated thermocouple inserted in the cavity.

Similar experiments were carried out with toluene and ethylbenzene at a single temperature (*ca.* 75°C). These yielded bimolecular rate constants as follows: toluene, $0.21 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (74.0°C); ethylbenzene, $3.0 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (75.8°C); cumene, $4.9 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (75.0°C). These figures, after statistical correction, form the basis of the relative reactivities at 75°C given in the Table.

Reactions of Acyl Nitroxides with Cyclohexane.—(a) A solution of *t*-butyl nitroxide (300 mg) in cyclohexane (30 cm³) was boiled under reflux until the green colour of the radical was discharged (140 h), and solvent was removed. The residue (260 mg) was separated into three fractions (p.l.c. silica gel–CH₂Cl₂), the most polar of which (52 mg) was identified as *O-benzoyl-N-t-butylhydroxylamine* by comparison with authentic material.¹ The least polar (107 mg) contained *NO*-dibenzoyl-*N-t-butylhydroxylamine* (3) and a compound believed to be *N-benzoyl-N-t-butyl-O-cyclohexylhydroxylamine*, in almost equal proportions. The intermediate fraction (55 mg) was the nearly pure *O*-cyclohexyl derivative [ν_{max} 1638 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.49 (s, 9 H, Bu^t), 0.5–2.3 (m, 10 H, 5 CH₂), 3.4 (broad, 1 H, >CHO–), and 7.05–7.65 (m, 5 H, Ph)]. The combined yield of this substance was *ca.* 30%.

(b) A solution of *t*-butyl 3,5-dinitrobenzoyl nitroxide¹ (1 g) in acid-free methylene chloride (3 cm³) was mixed with cyclohexane (25 cm³), and the resulting solution was boiled under reflux until the green colour was discharged (8 h). After cooling, the precipitated *N-t-butyl*dinitrobenzohydroxamic acid was removed, and evaporation of solvent then left a yellow residue which slowly crystallised. Crystallisation from hexane gave *N-(3,5-dinitrobenzoyl)-N-t-butyl-O-cyclohexylhydroxylamine* (6), m.p. 107°C [70%; ν_{max} (CCl₄) 1650 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.56 (s, 9 H, Bu^t), 0.5–2.3 (m, 10 H, 5 CH₂), 3.67 (broad, 1 H, >CHO–), and 8.6–9.0 (m, 3 H, aromatic) (Found: C, 55.7; H, 6.3; N, 11.8%. C₁₇H₂₃N₃O₆ requires C, 55.9; H, 6.3; N, 11.5%).

(c) A solution of the dinitrobenzoyl nitroxide (243 mg) and iodine (2.53 g) in cyclohexane (30 cm³) was boiled under reflux for 8 h, cooled, and the precipitated hydroxamic acid was removed. The remaining solution was washed with aqueous sodium thiosulphate (0.1M, $3 \times 50 \text{ cm}^3$), and water ($3 \times 50 \text{ cm}^3$), dried, and most of the solvent was removed. Examination of the residue by g.l.c. indicated the presence of cyclohexyl iodide (73%), and this was confirmed by spectroscopic comparison with authentic material.

*Reactions of Benzoyl *t*-Butyl Nitroxide with Alkenes*.—(i) *Cyclohexene*. A solution of the radical (425 mg) in benzene (10 cm³) was deoxygenated by the passage of nitrogen, and cyclohexene (10 cm³) was added dropwise whilst passage of nitrogen was continued. The mixture was stirred under N₂ at room temperature until the colour of the radical was discharged (30 min). After this, t.l.c. examination indicated the presence of *N-t-butylbenzohydroxamic acid*, and a new less-polar product. The hydroxamic acid was removed

(3 × 25 cm³ 2M-NaOH), and after washing the remaining solution with water and drying (MgSO₄), solvent was removed to leave a colourless viscous oil (300 mg, 98%) which was homogeneous on t.l.c., and had spectroscopic properties consistent with its formulation as *N*-benzoyl-*N*-*t*-butyl-*O*-cyclohex-2-enylhydroxylamine [ν_{\max} , 1 643 cm⁻¹; δ (CDCl₃) 1.53 (s, 9 H, Bu^t), 1.0–2.2 (m, 6 H, 3CH₂), 4.0 (m, 1 H, =CHO), 5.57 (m, 2 H, olefinic), and 7.1–7.6 (m, 5 H, Ph)].

(ii) *Norbornene*. A solution of freshly distilled norbornene (5 g) in benzene (8 cm³) was added to a stirred (N₂) solution of the nitroxide (500 mg) in benzene (2 cm³). After stirring at room temperature for 6 h, the colour of the radical was discharged. Evaporation of solvent and norbornene left a colourless viscous oil which contained at least two components of similar polarity (t.l.c.). P.l.c. (silica gel, 5% Et₂O in CH₂Cl₂) gave a partial separation, and from the major fraction colourless crystals of *trans*-2,3-*bis*-(*N*-benzoyl-*N*-*t*-butylamino-oxy)bicyclo[2.2.1]heptane (7) separated, m.p. 110 °C from ethanol [δ (CDCl₃) 1.45 (s, 9 H, Bu^t), 1.49 (s, 9 H, Bu^t), 0.2–2.0 (m, 8 H), 3.49 (t, H-3 *endo*, *J* ca. 2 Hz), 3.71 (dd, H-2 *exo*), and 7.2–7.6 (m, 10 H, 2 × Ph) (Found: C, 72.4; H, 7.7; N, 5.7%. C₂₉H₃₈N₂O₄ requires C, 72.8; H, 7.9; N, 5.8%). Repetition of the experiment and examination of the crude product by n.m.r. showed an additional doublet at δ 3.69 (*J* ca. 2 Hz) assigned to the 2,3-*exo-cis*-adduct. An unidentified product containing only aromatic protons was also present. Addition of a known quantity of dibenzyl, and n.m.r. peak integration indicated yields of ca. 63 and 17% for the *trans*- and *exo-cis*-adducts respectively.

(iii) *Norbornadiene*. A solution of the nitroxide (500 mg) in freshly distilled norbornadiene (5 g) and benzene (4 cm³) was stirred at room temperature (N₂) until the colour of the radical was discharged (1 h). Removal of the solvent gave a colourless oil (600 mg) which was separated into four fractions of slightly different polarities by p.l.c. (silica gel, 8% Et₂O–CH₂Cl₂). The least-polar fraction appeared (n.m.r.) to be a mixture of the two norbornenes (8) and (9), whilst the remaining three fractions were largely the tricyclic isomers (10) and (11) in differing proportions. Attempts to isolate the individual isomers were, however, unsuccessful, and no crystalline products were obtained. Key features in the n.m.r. spectra (CDCl₃, 50 °C) were as follows. *cis-exo*-Adduct (8): δ 1.47 (s, Bu^t), 0.8 (broad q, 1 H, H-7), 2.51 (t, 2 H, H-1, 4, *J* 2 Hz), 3.77 (d, 2 H, H-5, 6, *J* 2 Hz), and 5.75 (t, 2 H, vinyl, *J* 2 Hz); *trans*-adduct (9): δ 1.47 (s, Bu^t), 0.6 (d, 1 H, H-7 *anti*, *J* 9 Hz), 0.93 (broad d, 1 H, H-7 *syn*, *J* 9 Hz), 2.4 and 2.58 [both broad s, 1 H, H-1 and H-4 respectively (from decoupling experiments)] 4.2 [dd, 1 H, H-6 (*exo*), *J* 3.5 and 2 Hz], 3.60 [t, 1 H, H-5 (*endo*), *J* 2 Hz (coupling to H-2 and H-7 *syn*)], and 5.22 and 5.5 (both dd, 2 H, H-2 and 3, both *J* ca. 5.5 and 3 Hz); *cis-exo*-nortricyclene (10): δ 1.36 (s, Bu^t), 3.31 (broad s, =CHO); unsymmetrical nortricyclene (11): δ 1.35 and 1.42 (both s, Bu^t), and 3.50 and 3.97 (both broad s, =CHO).

No evidence for products other than these four could be added from the spectra. Repetition of the experiment and integration of the spectrum of the total reaction mixture after addition of a known amount of dibenzyl as internal reference indicated the following yields: (8), 10%; (9), 19%; (10), 28%; (11), 38%.

(iv) *Styrene*. The calculated quantity of styrene (0.13 g) was added to a stirred solution of the radical (0.49 g) in

benzene (10 cm³). The solution was boiled under reflux until the colour of the radical was discharged, solvent was removed, and a major product (0.47 g, 76%) was isolated by p.l.c. as in (ii). The spectra of the product, a viscous oil, were consistent with its formulation as 1,2-*bis*-(*N*-benzoyl-*N*-*t*-butylamino-oxy)-1-phenylethane [ν_{\max} , 1 640 cm⁻¹; δ (CDCl₃, 35 °C) 1.30 (s, 9 H, Bu^t), 1.38 (s, 9 H, Bu^t), 3.20–4.35 (m, 3 H, CHCH₂), and 6.87–7.68 (m, 15 H, 3 Ph)].

(v) α -*Methylstyrene*. In an experiment similar to that with styrene, a solid product was obtained which after crystallisation from aqueous methanol had m.p. 116–116.5 °C (59%). This was identified as 1,2-*bis*-(*N*-benzoyl-*N*-*t*-butylamino-oxy)-1-methyl-1-phenylethane [ν_{\max} , (Nujol) 1 650 cm⁻¹; δ (CDCl₃) 1.09 (s, 3 H, Me), 1.12 (s, 9 H, Bu^t), 1.22 (s, 9 H, Bu^t), 3.55 (ABq, 2 H, CH₂), and 7.15–7.5 (m, 15 H, 3 Ph) (Found: C, 74.6; H, 7.7; N, 5.4%. C₃₁H₃₈N₂O₄ requires C, 74.1; H, 7.6; N, 5.6%).

(vi) *Stilbenes*. Reactions with the stilbene isomers were carried out as for styrene. The reactions were very slow, and in each case self-reaction of the nitroxide gave some *NO*-dibenzoyl-*N*-*t*-butylhydroxylamine (3) as well as the expected adduct, m.p. 178–179 °C [ν_{\max} , (Nujol) 1 683 cm⁻¹; δ (CDCl₃) 1.30 (s, 18 H, Bu^t), 4.72 (s, 2 H, CH), and 6.65–7.45 (m, 20 H, Ph) (Found: C, 76.2; H, 7.2%. C₃₆H₄₀N₂O₄ requires C, 76.6; H, 7.1%). The yields of adduct were, from *trans*-stilbene ca. 30%, and from *cis*-stilbene, ca. 55%.

Reactions with Other Substrates.—(i) *Diphenylmethane*. Diphenylmethane (558 mg) was added to a solution of the benzoyl nitroxide (1.275 g, 2 equiv.) in dry benzene (15 cm³) and the mixture was refluxed for 2 h. Dilution with diethyl ether (35 cm³), and extraction with 2M-NaOH in the usual way gave *N*-*t*-butylbenzohydroxamic acid (585 mg, 91%) identical with authentic material. The remaining ethereal solution was dried, and solvent was removed to leave a solid which crystallised from hexane–CH₂Cl₂ (6 : 1) as colourless prisms, m.p. 149–150 °C. This was identified as *O*-benzhydryl-*N*-benzoyl-*N*-*t*-butylhydroxylamine (12) [1.034 g, 87%; ν_{\max} , (Nujol) 1 630 cm⁻¹; δ (CDCl₃) 1.46 (s, 9 H, Bu^t), 5.56 (s, 1 H, CH), and 6.88–7.27 (m, 15 H, 3Ph) (Found: C, 79.9; H, 7.2; N, 3.9%. C₂₄H₂₅NO₂ requires C, 80.2; H, 7.0; N, 3.9%).

(ii) *Cyclohexa-1,4-diene*. The diene (distilled from triphenylphosphine–MgSO₄, 94 mg) was added to a solution of the benzoyl nitroxide (127.5 mg) in oxygen-free CDCl₃ (0.5 g). There was a rapid exothermic reaction. Integration of the n.m.r. spectrum of the products, assuming quantitative formation of *N*-*t*-butylbenzohydroxamic acid (2), indicated a 95% yield of benzene. Examination by g.l.c., comparing the benzene and unchanged diene, indicated a yield of 100 ± 3%. Solvent removal afforded *N*-*t*-butylbenzohydroxamic acid (124.8 mg, 97%).

(iii) 9,10-*Dihydroanthracene*. A solution of the hydrocarbon (187 mg) in dry diethyl ether (10 cm³) was added to the radical (398 mg, 1.99 equiv.). Rapid decolourisation ensued, and removal of solvent then left an oil which partially crystallised. Separation of the products by p.l.c. (silica gel, CH₂Cl₂) gave unchanged 9,10-dihydroanthracene containing a trace of anthracene (19 mg), *N*-*t*-butylbenzohydroxamic acid (198 mg, 98%) and 9-(*N*-benzoyl-*N*-*t*-butylamino-oxy)-9,10-dihydroanthracene (13) as colourless prisms from hexane, m.p. 126–128 °C (decomp.) (351 mg, 91% before crystallisation). The compound was unstable and consistently gave a low carbon analysis (Found: C, 79.3; H, 6.8; N, 3.5%. C₂₅H₂₅NO₂ requires C, 80.8;

H, 6.8; N, 3.8%), ν_{\max} (Nujol) 1 639 cm^{-1} ; $\delta(\text{CDCl}_3)$ 1.48 (s, 9 H, Bu^t), 3.31 (broad s, 2 H, CH_2), 5.48 (broad s, 1 H, CH), and 6.9—7.3 (m, 13 H, aromatic).

(iv) *Aldehydes*. The general procedure is typified by the reaction of benzaldehyde. A solution of this aldehyde (121 mg, 1.14 mmol) and the benzoyl nitroxide (438 mg, 2.28 mmol) in benzene (25 cm^3) was boiled under reflux until the green colour was discharged (3½ h). After cooling, diethyl ether (30 cm^3) was added, and the mixture was washed with 0.5M-NaOH (3 × 25 cm^3), water (2 × 20 cm^3), saturated aqueous NaHSO_3 (2 × 10 cm^3), water, and was then dried (Na_2SO_4). The alkaline washings were acidified and extracted with diethyl ether to give *N*-*t*-butylbenzohydroxamic acid (183 mg, 83%). Evaporation of the dried organic phase left a solid which, following crystallisation from hexane- CH_2Cl_2 (8:1), was indistinguishable from a pure specimen of *NO*-dibenzoyl-*N*-*t*-butylhydroxylamine¹ (289 mg, 85%).

Similar reactions with substituted benzaldehydes proceeded as follows. 4-Dimethylaminobenzaldehyde: reaction time 70 min, product [*p*- $\text{Me}_2\text{NC}_6\text{H}_4\text{CO}_2\text{N}(\text{Bu}^t)\text{COPh}$], m.p. 160—161 °C, 87%. 4-Methoxybenzaldehyde: reaction time 3 h, product [*p*- $\text{MeOC}_6\text{H}_4\text{CO}_2\text{N}(\text{Bu}^t)\text{COPh}$], oil, 91%. 4-Bromobenzaldehyde: reaction time 11½ h, product [*p*- $\text{BrC}_6\text{H}_4\text{CO}_2\text{N}(\text{Bu}^t)\text{COPh}$], m.p. 88—89 °C, 87%. 4-Nitrobenzaldehyde: reaction time 24 h, product [*p*- $\text{O}_2\text{NC}_6\text{H}_4\text{CO}_2\text{N}(\text{Bu}^t)\text{COPh}$], m.p. 113—114 °C, 77%. All products had spectroscopic properties fully in accord with the assigned structure. A similar reaction with acetalde-

hyde gave *O*-acetyl-*N*-benzoyl-*N*-*t*-butylhydroxylamine, m.p. 61—61.5 °C (81%) identical with authentic material.¹

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