

REACTION OF *t*-BUTOXY RADICALS WITH NORBORNADIENE

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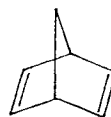
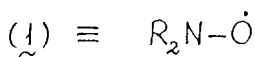
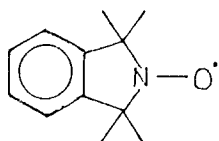
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95 percent of the reaction of t-butoxy radicals with norbornadiene occurs by radical addition followed by rearrangement to nortricycyl and 7-t-butoxynorbornenyl products; the remainder includes a novel radical rearrangement involving a 1,3-H shift and some radical abstraction observed for the first time.

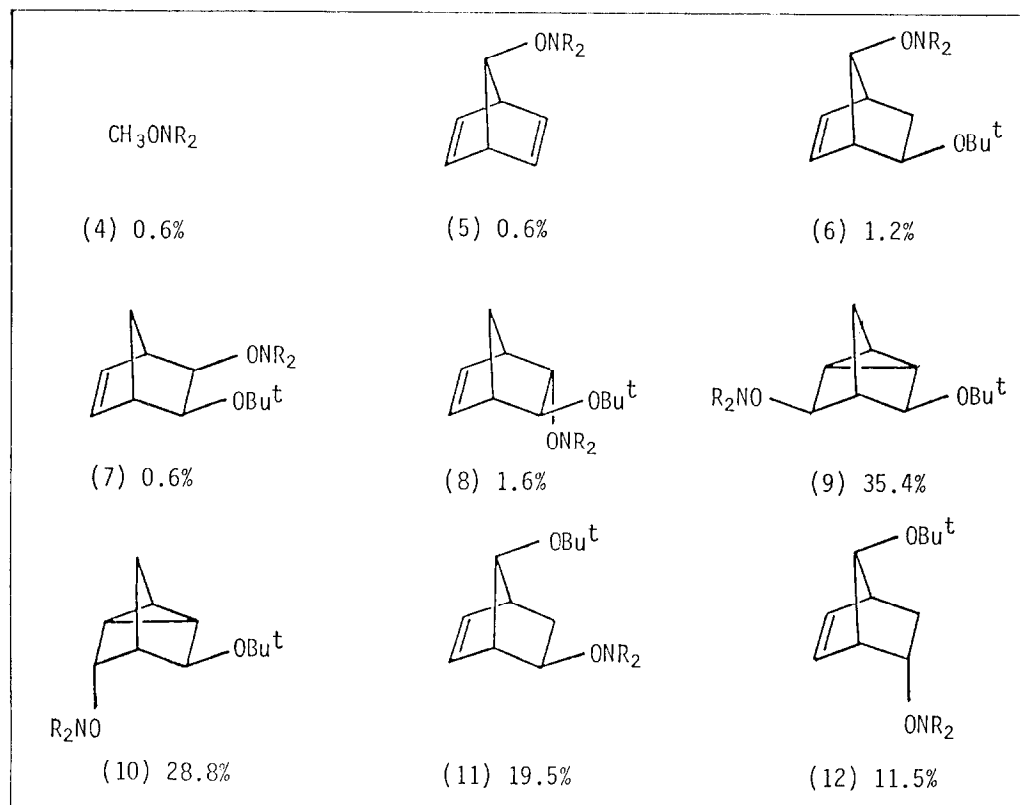
The regioselectivity and stereoselectivity of the reactions of oxy radicals with olefins can be conveniently studied using the scavenger 1,1,3,3-tetramethylisindolin-2-yloxy (1). This nitroxide radical trap efficiently scavenges carbon-centred radicals to produce stable alkoxy amine products which may be readily isolated and identified. Both major and minor reaction pathways can be determined and such studies¹⁻⁵ have been invaluable in elucidating the complex processes involved in the initiation of free radical polymerisation. In the present study, (1) has been employed to investigate the reaction of *t*-butoxy radicals with norbornadiene (2). In previous investigations of this reaction⁶, interest has centred on the norbornenyl-nortricycyl radical rearrangement and the techniques have provided information on only the major processes taking place. By contrast, the use of (1) has allowed a detailed



picture of both major and minor pathways to emerge.

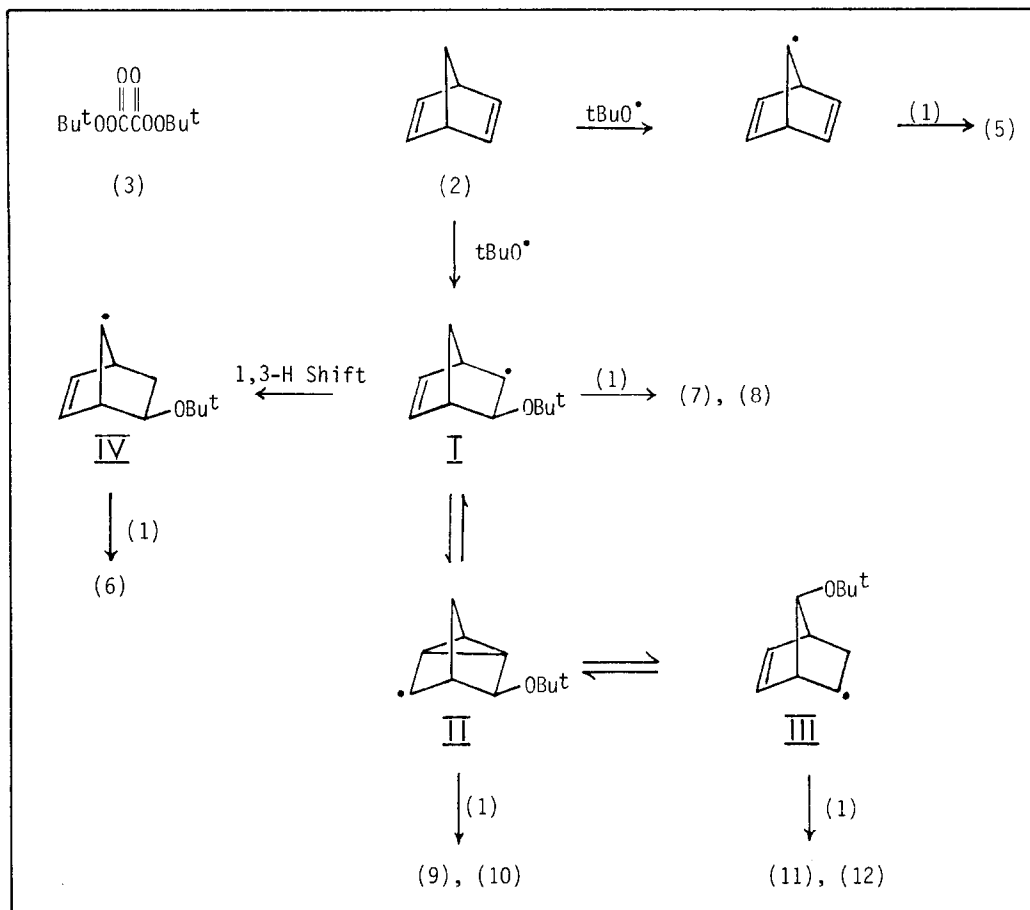
t-Butoxy radicals were generated⁷ by thermolysis of di-t-butyl peroxalate (3). Thus, a solution of (3, 234 mg, 1 mmole) and (1, 419 mg, 2.2 mmole) in freshly purified norbornadiene (2, 10 ml, 100 mmole) was degassed by freeze/thaw cycles, sealed under vacuum (<0.001 torr) and heated at 60°C for 70 min. Following separation and quantitative analysis of the reaction mixture by reverse-phase h.p.l.c., the products were identified by ¹³C and ¹H n.m.r.

The relative yields of the alkoxyamine adducts⁸ (4)-(12) are given in scheme 1 and the overall reaction scheme is shown in scheme 2.



Scheme 1

In keeping with previous observations, the t-butoxy radicals undergo a small fraction of β -scission prior to reaction with (2) resulting in adduct (4) and acetone. Previous reports on radical reactions^{6,9} with (2) have claimed that radical addition to the double bond is the only detectable process. In contrast we have found that a small but measurable amount of abstraction (0.6%) occurs at the homoallylic position to produce adduct (5). However, 98% of the radical reactions are attributable to addition reactions leading to a range of adducts (6) to (12). Only 2.2% of these, (7) and (8), arise from simple 1,2-addition, the majority result from radical rearrangements of the initially formed norbornenyl radical I to give the nortricycyl radical II (64%) and the 7-t-butoxynorbornenyl radical III (31%) (Scheme 2).



The latter radical arises from ring-opening of the nortricyclic radical II and although this type of process has formerly been regarded as rare⁶ the present results clearly show that it can play an important role in the overall reaction. The results also indicate that the rate of isomerisation I → II → III is extremely fast since the rate constant for the reaction of (1) with carbon-centred radicals is of the order of $10^9 \text{M}^{-1} \text{s}^{-1}$. The ratio of adduct yields from the nortricyclic and norbornenyl radicals, 1.87, is close to the equilibrium value^{6b,10} of 1.86, indicating that the relative proportions of these radicals is under thermodynamic control.

Probably the most unusual feature of the reaction is the formation of adduct (6)¹¹. The simplest mechanism one can postulate for this product is a 1,3-H shift from the methylene group of I to give radical IV followed by trapping with (1). H transfer reactions are normally only expected when there is close to colinear alignment of the atoms in the transition state¹², which is clearly not possible in this case. However, some 1,3-H shifts have been reported^{6b} and we tentatively suggest that this system provides another example. There have been no previous reports of rearrangements of the type I → IV.

Finally, it is worth noting that *t*-butoxy only adds to the exo face of the norbornadiene.

This is presumably due to a combination of steric and electronic effects. Electronic effects almost certainly account for the exclusive formation of (6) from radical IV, while steric effects probably account for the higher proportion of endo trapping of radical I (ratio of endo:exo trapping, almost 3:1). This is in contrast to the preferred exo trapping of II and of III.

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References and notes

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- Spectral data for product (6):

^{13}C n.m.r. (CDCl_3/TMS): 145.3 (C-3'a, C-7'a); 136.8 (C-3); 129.7 (C-2); 127.2 (C-5', C-6'); 121.6 (C-4', C-7'); 87.0 (C-7); 84.0 (C-5); 73.4 (OCMe_3); 67.5 (C-1', C-3'); 53.1 (C-4); 45.7 (C-1); 32.2 (C-6); 30.3, 25.5 (4 CH_3 groups) and 28.6 ($\text{OC}(\text{CH}_3)_3$).

^1H n.m.r. (CDCl_3/TMS): 7.18 (m, 2H, H-5', H-6'); 7.05 (m, 2H, H-4', H-7'), 6.14 (m, 1H, H-3, J ~ 5.7, 2.8, 0.9 Hz); 5.91 (m, 1H, H-2, J ~ 5.7, 3.1 Hz); 4.22 (br.s., 1H, H-7); 3.85 (ddd, 1H, H-5-endo, J ~ 6.7, 4.3, 0.8 Hz); 3.02 (m, 1H, H-4); 2.69 (m, 1H, H-1); 1.62 (m, 2H, H-6); 1.48, 1.37 (broad hump, 12H, 4 CH_3 protons) and 1.22 (s, 9H, $(\text{CH}_3)_3\text{C}$ -).

(note: primed numbers refer to isoindolin ring)
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