

A 1,3-Nitro Migration in the Reaction of Nitrogen Dioxide with 2-t-Butyl-4,6-dimethyl-4-nitrocyclohexa-2,5-dienone

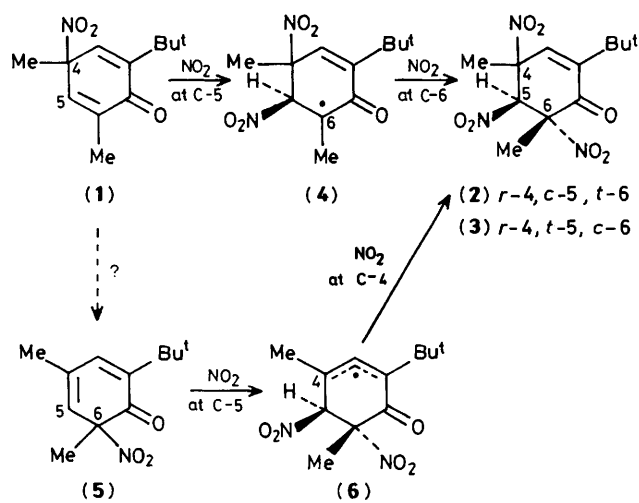
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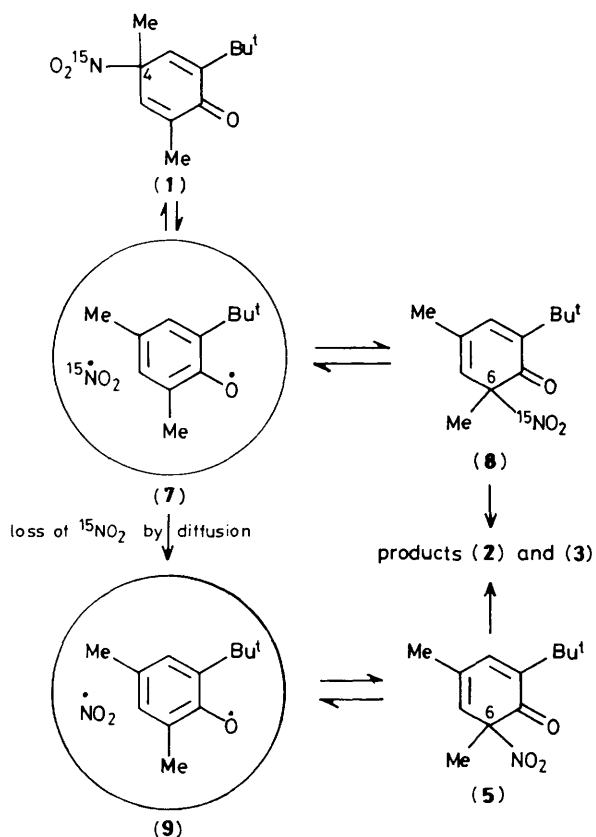
The formation of the 2-t-butyl-4,6-dimethyl-4,5,6-trinitrocyclohex-2-enones (2) and (3) on reaction of 2-t-butyl-4,6-dimethyl-4-nitrocyclohexa-2,5-dienone (1) with nitrogen dioxide proceeds via 4,5-addition of nitrogen dioxide to the 6-nitrocyclohexa-2,4-dienone (5), the product of a 1,3-nitro migration.

The formation of the 4,5,6-trinitrocyclohex-2-enones (2) and (3) on reaction of the 4-nitrocyclohexa-2,5-dienone (1) with nitrogen dioxide¹ could occur by 5,6-addition of nitrogen dioxide via the radical species (4) (Scheme 1). Alternatively, it appeared possible that the reaction involved 4,5-addition of nitrogen dioxide to the 6-nitrocyclohexa-2,4-dienone (5); in this case, the second addition of nitrogen dioxide to the intermediate (6) at C-4 would be preferred for steric reasons. The conversion of the 4-nitrodienone (1) into the 6-nitrodienone (5) formally involves nitro group migration from C-4 to C-6. Such a migration has been demonstrated to occur, and by a homolytic mechanism, for a substrate in which the rearrangement terminus is unsubstituted.² Although this type of migration to an occupied ring position has been inferred from product structures,³ no direct evidence for such a nitrodienone rearrangement has been reported. We now report the results of a ¹⁵N-labelling study of the reaction of the 4-nitrodienone (1) with nitrogen dioxide to give trinitrocyclohex-2-enones (2) and (3).

The labelled 4-nitrodienone (1), prepared by nitration of



Scheme 1



Scheme 2

the corresponding phenol with [^{15}N]nitric acid (95% ^{15}N), gave ^1H n.m.r. spectra consistent with the presence of the ^{15}N label at C-4 {(300 MHz, CDCl_3) δ 1.86 [d, $J(\text{Me}, ^{15}\text{N})$ 3.4 Hz, 4-Me] and 1.94 [d, $J(\text{Me}, 5\text{-H})$ 1.5 Hz, 6-Me]}. Reaction of

the ^{15}N -labelled 4-nitrodienone (1) with nitrogen dioxide in benzene for 2 h (cf. ref. 1) gave the C-4-epimeric trinitro ketones (2) and (3), which were separated and their ^1H n.m.r. spectra examined: trinitro ketone (2), ^1H n.m.r. (300 MHz, CDCl_3) δ 1.26 (Bu^t), 1.95 (s, 6-Me), 1.95 [d, $J(\text{Me}, ^{15}\text{N})$ 3.6 Hz, 6-Me], 2.09 (s, 4-Me), 6.11 (s, 5-H), and 6.74 (s, 3-H); ^{15}N -incorporation estimated from 6-Me signal, $40 \pm 5\%$; trinitro ketone (3), ^1H n.m.r. (300 MHz, CDCl_3) δ 1.25 (Bu^t), 1.94 (s, 4-Me), 1.95 (s, 6-Me), 1.95 [d, $J(\text{Me}, ^{15}\text{N})$ 3.0 Hz, 6-Me], 6.53 (s, 3-H), and 6.97 (s, 5-H); ^{15}N -incorporation estimated from 6-Me signal, $37 \pm 7\%$. The assignment of signals reported above was confirmed by appropriate difference nuclear Overhauser effect (n.O.e.) experiments for unlabelled compound (2); for compound (3) HETCOR experiments led to a reassignment of the signals due to 3- and 5-H (cf. ref. 1), and difference n.O.e. experiments allowed the assignment of the methyl resonances.

The results reported above may be interpreted in terms of Scheme 2. This Scheme is analogous to that reported earlier² for substrates lacking substituents at C-2 and C-6. Homolysis of ^{15}N -labelled nitrodienone (1) gives the radical pair in a solvent cage (7). Exchange of [^{15}N]nitrogen dioxide with the excess of unlabelled nitrogen dioxide in the system gives radical pair (9). Recombination in these two radical pairs would give the labelled and unlabelled 6-nitrodienones (8) and (5) respectively, which then undergo 4,5-addition of nitrogen dioxide to give the products (2) and (3), labelled exclusively at C-6.

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References

- 1 M. P. Hartshorn, W. T. Robinson, K. H. Sutton, and J. Vaughan, *Aust. J. Chem.*, 1985, **38**, 161.
- 2 C. E. Barnes and P. C. Myhre, *J. Am. Chem. Soc.*, 1978, **100**, 973.
- 3 M. J. Gray, M. P. Hartshorn, J. Vaughan, and G. J. Wright, *Aust. J. Chem.*, 1985, **37**, 2027; and references cited therein.