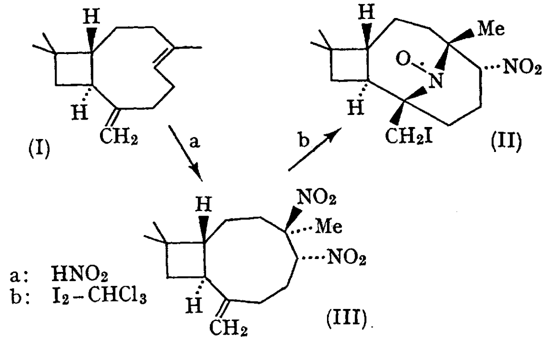
The Structure and Absolute Stereochemistry of Caryophyllene "Iodo-nitrosite": a Stable Nitroxide Radical

By D. M. HAWLEY, J. S. ROBERTS, G. FERGUSON,* and A. L. PORTE

(*Chemistry Department, University of Glasgow, Glasgow, W.2*)

AN important derivative previously used in the characterisation of caryophyllene (I) was the blue crystalline nitrosite,[1] the structure of which has never been satisfactorily established.[2] In the course of a re-examination of the chemistry of this compound a stable crystalline "iodo-nitrosite" was prepared by treatment of the nitrosite with iodine in chloroform solution at room temperature using Deussen's method.[1] The ^{1}H n.m.r. spectrum of the "iodo-nitrosite" when examined over the range $0 \leqslant \tau \leqslant 10$ exhibited only a broad hump in the region $7 \leqslant \tau \leqslant 9$ with no visible fine structure, indicating that a paramagnetic species might be present. A 0·001 M solution of the compound in a 3 : 2 chloroform : toluene mixture, at 295° K, gave a very intense paramagnetic resonance spectrum consisting of a 1 : 1 : 1 triplet [isotropic *g*-factor = 2·0062 ± 0·0002; isotropic hyperfine coupling constant, a (^{14}N) = 15·3 ± 0·1 gauss]. No further hyperfine splitting of this spectrum could be detected on further dilution even after extensive degassing of the solution. The form of this paramagnetic resonance spectrum and its magnetic parameters are almost identical with those exhibited, under the same experimental conditions, by the di-t-butyl nitroxide radical, $(Me_3C)_2\dot{N}O$ [isotropic *g*-factor = 2·0063 ± 0·0002; isotropic hyperfine coupling constant, a (^{14}N) = 15·5 ± 0·1 gauss], and are quite different from the parameters expected from the various kinds of radicals which may be derived from compounds of the form $R{\cdot}NO_2$,[3] or from iminoxy-radicals[4] of the type $R_2C = \dot{N}O$.



a: HNO_2
b: I_2-$CHCl_3$

The "iodo-nitrosite" therefore belongs to the relatively new class of stable aliphatic nitroxide radicals.[5] We have carried out a single-crystal *X*-ray analysis which unambiguously establishes its structure and absolute stereochemistry as (II) and thus confirms Barton and Nickon's earlier assignment[6] of the absolute configuration of (I) for caryophyllene. From structure (II) and spectroscopic and chemical[7] evidence, we infer structure (III) for the parent caryophyllene nitrosite. The formation of the nitroxide radical probably involves the addition of I$^\bullet$ to the *exo*-methylene group in (III) thus forming a tertiary alkyl radical which in turn undergoes transannular addition to the nitroso-group generating the nitroxide radical. This mechanism finds analogy in that established for the intermolecular addition of alkyl and alkoxy-radicals to a nitroso-group.[8]

The orange-red crystals of the nitroxide radical are orthorhombic, space group $P2_12_12_1$, with 4 molecules of $C_{15}H_{24}N_2O_3I$ in a unit cell of dimensions $a = 6{\cdot}78$, $b = 8{\cdot}24$, $c = 30{\cdot}49$ Å. About 1100 X-ray intensity data were obtained from a crystal rotating about axis a on our Hilger and Watts linear diffractometer[9] and the structure was elucidated by the heavy-atom method.[10] The absolute configuration was determined from a consideration of the differences in intensity of 18 Bijvoet pairs[11] of reflexions measured with Mo-K_α radiation. The reliability index, R, is now 0·12; refinement of the atomic parameters by least-squares calculations† is in progress.

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