

## Bis-(6,6-dimethylnorpinane-2,2-diyl) Diperoxide

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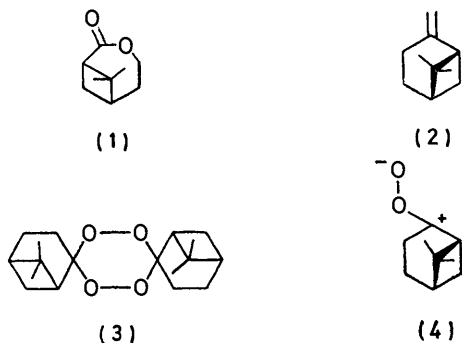
The substance  $C_9H_{14}O_2$  obtainable from ozonolysis of pin-2(10)-ene and previously formulated as 7,7-dimethyl-3-oxabicyclo[4,1,1]octan-2-one (1) is shown to be a diastereoisomer (6) of bis(6,6-dimethylnorpinane-2,2-diyl) diperoxide.

IN 1928 Brus and Peyresblauques described<sup>1</sup> the isolation in low yield of a crystalline substance,  $C_9H_{14}O_2$ , m.p. 125–126°, from ozonolysis of (–)-pin-2(10)-ene and formulated it as the lactone (1). Its formation under these conditions seemed to us unlikely and we have therefore re-examined the nature of this product.

Ozonolysis of (–)-pin-2(10)-ene (2) under the published conditions and chromatography of the residue from steam distillation afforded a non-polar fraction in 1.5–2.6% yield. Fractional crystallisation of this material from ethanol furnished a pure substance, m.p. 131–132°,  $[\alpha]_D -28.9^\circ$ , and a mixture, m.p. 83–100°,  $[\alpha]_D -22.3^\circ$ , both giving analytical figures corresponding to  $C_9H_{14}O_2$ . We assume that the former is the material isolated by Brus and Peyresblauques.

The absence in the i.r. spectrum of carbonyl and hydroxy-absorption and the presence of strong bands at 1012 and 1018  $cm^{-1}$  (cf. ref. 2) immediately eliminates the lactone (1) from consideration and indicates the diperoxide (3),  $(C_9H_{14}O_2)_2$ , as the likely product.

The mass spectrum lacked a molecular ion, in accordance with previous studies<sup>3</sup> of diperoxides, but it did show minor fragment ions  $(M - H_2O_2)^+$ ,  $(M - H_2O_2 - H_2O)^+$ , and  $(M - H_2O_2 - H_2O - CH_3)^+$ . The major ions were those of the parent ketone<sup>3,4</sup> (nopinone)  $[M^+$



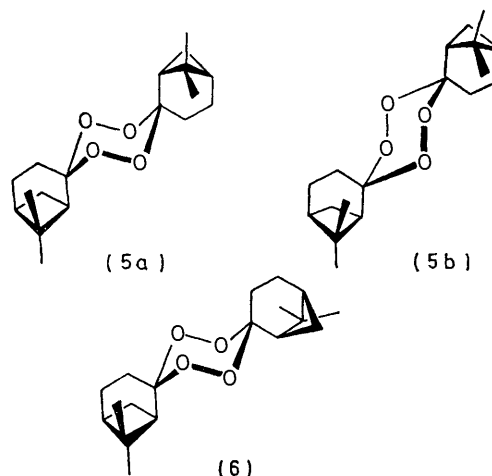
and  $(M + 1)^+$  as in the case of cyclohexanone diperoxide<sup>3</sup>] and its expected fragmentation products. The molecular weight was found by the thermistor drop method to be  $305 \pm 2$  [Calc. for  $(C_9H_{14}O_2)_2$ : 308].

Chemical support for structure (3) came from formation of nopinone (6,6-dimethylnorpinan-2-one) either on thermolysis<sup>4</sup> or reaction with toluene-*p*-sulphonic acid in boiling benzene and of  $\alpha$ -nopinol (6,6-dimethylnorpinan-2 $\alpha$ -ol) (as well as of nopinone) from reduction with lithium aluminium hydride.

<sup>1</sup> G. Brus and G. Peyresblauques, *Compt. rend.*, 1928, **187**, 984; see 'The Terpenes,' ed. J. L. Simonsen, 2nd edn., vol. 11, Cambridge University Press, 1957, p. 199.

<sup>2</sup> M. S. Kharasch and G. Sosnovsky, *J. Org. Chem.*, 1958, **23**, 1322.

The formation of the diperoxide presumably proceeds via the Criegee zwitterion (4),<sup>5</sup> which can dimerise to afford two diastereomeric diperoxides (5) and (6). The *syn*-isomer (5) has a two-fold axis of symmetry and can



exist as two distinct conformers (5a) and (5b). The *anti*-isomer (6) lacks a formal symmetry element and its conformational inversion is degenerate. We consider that the compound of m.p. 131–132° is one diastereomer (6) and the mixture, m.p. 83–100°, is enriched with respect to the other (5). This is borne out by the combustion analyses and the virtual identity of the i.r. and mass spectra of the two materials. The pure diperoxide was assigned the *anti*-configuration (6) on the basis of its n.m.r. spectral properties.<sup>6</sup>

The 100 MHz spectrum ( $CDCl_3$ ; 33.5°) shows the methyl signals as two broadened singlets (6H each) at  $\delta$  0.96 and 1.27. At 220 MHz and –56° in  $CDCl_3$ , four methyl signals of equal intensity (3H each) are observable at  $\delta$  0.92, 0.94, 1.21, and 1.29. This behaviour is expected for the diastereomer (6). It has four methyl groups in different magnetic environments, but since there is only one effective conformer (inversion is degenerate), the methyl signals must necessarily be of equal intensity (3H each). The diastereomer (5) has two non-equivalent methyl groups (two-fold axis of symmetry) in each of two conformers (5a) and (5b), so that four methyl signals would be expected from the equilibrium mixture. However, only if the equilibrium were equally populated by the two conformers would the four signals be of equal intensity. If this were the case in  $CDCl_3$ , then change to

<sup>3</sup> T. Ledaal, *Tetrahedron Letters*, 1969, 3661.

<sup>4</sup> P. R. Story, D. D. Denson, C. E. Bishop, B. C. Clark, and J.-C. Farine, *J. Amer. Chem. Soc.*, 1968, **90**, 817.

<sup>5</sup> R. Criegee, *Record Chem. Progr.*, 1957, **18**, 111.

<sup>6</sup> See R. W. Murray, P. R. Story, and M. L. Kaplan, *J. Amer. Chem. Soc.*, 1966, **88**, 526.

another solvent,\* with an attendant change in the entropy of the solute-solvent complex, should change the position of the equilibrium and hence give rise (barring accidental equivalence) to two pairs of methyl signals of unequal intensity. The 220 MHz spectrum in  $C_6D_5 \cdot CD_3$  at  $-55^\circ$ , however, still shows methyl signals of equal intensity (3H each) at  $\delta$  1.19 and 1.00 and a barely resolved 6H singlet (two superimposed 3H signals) at  $\delta$  0.92. We therefore favour the configuration (6) for the isomer of m.p. 131—132°.

#### EXPERIMENTAL

*General.*—The following instruments were used: Perkin-Elmer 225 (i.r.); Varian HA 100 (n.m.r.); A.E.I. MS 9 (mass spectra) (the 220 MHz n.m.r. spectra were obtained by courtesy of the Physico-Chemical Measurement Unit, Harwell); Pye-Argon and Perkin-Elmer F11 (g.l.c.). The molecular weight of the diperoxide (6) was determined with a Mechrolabs Vapour Pressure Osmometer model 301A (benzil in  $CCl_4$  as standard).

Merck Kieselgel G was used for analytical and preparative t.l.c. Microanalyses were performed by J. M. L. Cameron and his staff.

*Ozonolysis of (-)-Pin-2(10)-ene.*—(a) (-)-Pin-2(10)-ene ( $[\alpha]_D -21^\circ$ ;  $n_D^{22.5} 1.4820$ ; 3.26 g) in AnalaR chloroform (20 ml) was ozonised for 3 h at  $0^\circ$  and then left for 16 h. Steam distillation left a semicrystalline residue which was taken up in ether; the solution was washed with aqueous sodium hydrogen carbonate and water and dried. Solvent removal and chromatography of the residue over grade O alumina afforded [with benzene-light petroleum (1:3)] crystalline material (96 mg, 2.6%) of m.p. 114—127°, homogeneous on t.l.c. in benzene ( $R_F$  0.87), which after five crystallisations from aqueous ethanol afforded *bis*-(6,6-dimethylnorpinane-2,2-diyl) diperoxide (6), m.p. 131—132°,  $[\alpha]_D -28.9^\circ$ , *m/e* 274 (5%), 256 (6), 241 (3), 139 (11), 138 (13), 123 (12), 110 (15), 109 (21), 83 (100), 81 (52), 55 (88), 44 (91),

\* We thank Dr. D. D. MacNicol for this suggestion.

<sup>7</sup> S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, 1954, **77**, 3054.

<sup>8</sup> O. Wallach, *Annalen*, 1907, **356**, 227.

and 41 (94) (Found: C, 70.2, 70.2; H, 9.25, 9.1.  $C_9H_{14}O_2$  requires C, 70.1; H, 9.15%).

A six-stage fractional crystallisation gave a head crop of m.p. 131—132° and a tail crop of m.p. 83—100°,  $[\alpha]_D -22.3^\circ$  (Found: C, 70.25; H, 9.25%).

(b) (-)-Pin-2(10)-ene (8.0 g) was ozonised as in (a) and the steam-volatile material (2.35 g) was recovered with ethyl acetate. T.l.c. showed one major product. Pure nopinone (200 mg),  $n_D^{22} 1.4765$  (lit.,<sup>7</sup>  $n_D^{25} 1.4769$ ), single peak on 1% SE 30, was obtained by a combination of column and thin-layer chromatography. The semicarbazone had m.p. 185—187° (lit.,<sup>8</sup> 188°).

*$\alpha$ -Nopinol.*—Obtained in 50% yield by the published method,<sup>8</sup>  $\alpha$ -nopinol had m.p. 101—102° (lit.,<sup>7</sup> 101.5—102°), single peak on 1% QF1. G.l.c. of the mother liquors from crystallisation of  $\alpha$ -nopinol showed no evidence of  $\beta$ -nopinol.

*Reduction of the Diperoxide (6).*—The diperoxide (6) (102 mg) in dry tetrahydrofuran (THF) (5 ml) was added to lithium aluminium hydride (200 mg) in dry THF (15 ml) and the suspension was refluxed for 5.5 h. Work-up as usual and preparative layer chromatography (benzene-chloroform, 1:1) afforded  $\alpha$ -nopinol (38 mg), m.p. (from pentane-ethyl acetate) 101—101.5°, mixed m.p. with authentic  $\alpha$ -nopinol, 100.5—101°, i.r. spectrum identical with that of  $\alpha$ -nopinol. G.l.c. of the total reaction product indicated the presence of nopinone (<5%), but no  $\beta$ -nopinol.

*Pyrolysis of the Diperoxide (6).*—The diperoxide (6) (21 mg) was slowly heated in a micro-sublimation apparatus at 30 mmHg, the temperature being allowed to rise to 220°; a negligible residue then remained. The distillate collected in two zones consisted of nopinone and unchanged diperoxide (6), both identical (t.l.c. and g.l.c.) with authentic samples.

*Reaction of the Diperoxide (6) with Toluene-p-sulphonic Acid in Benzene.*—The diperoxide (160 mg) and toluene-p-sulphonic acid (10 mg) were refluxed in dry AnalaR benzene (25 ml). G.l.c. and t.l.c. monitoring showed that ca. 15% of nopinone was present after 0.5 h but that after 4 h, when all diperoxide had reacted, only 5% of nopinone survived.

[2/2066 Received, 1st September, 1972]