Synthesis of Racemic Seychellene based upon Intramolecular Diels–Alder Addition of a Cyclohexadienone Derivative

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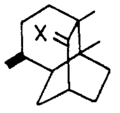
Summary Pyrolysis of the *N*-oxide of 6-(5-dimethylamino-3-methylpentyl)-5,6-dimethylcyclohexa-2,4-dienone gives a tricyclic ketone which on hydrogenation yields racemic norseychellanone.

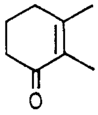
SEYCHELLENE (Ia) is a tricyclic sesquiterpene isolated from patchouli oil,[1] containing a bicyclo[2,2,2]octane system.



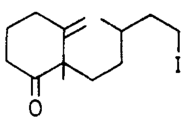
(I)

a; X = CH_2

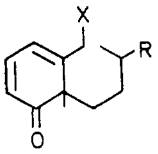
b; X = O



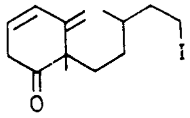
(II)



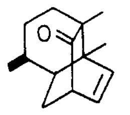
(III)



(IV)



(V)



(VI)

a; R = $(CH_2)_2I$, X = Br

b; R = $(CH_2)_2I$, X = H

c; R = $(CH_2)_2NMe_2$, X = H

d; R = $(CH_2)_2\underset{\overset{\downarrow}{O}}{N}Me_2$, X = H

e; R = $CH=CH_2$, X = H

Recently two syntheses of this sesquiterpene have been described,[2] both of which involve the stepwise construction of the tricyclic structure *via* bicyclic intermediates.

We report a total synthesis of racemic seychellene which involves as the key step the one-step construction of the tricyclic framework based upon the intramolecular Diels–Alder addition of a monocyclic cyclohexadienone derivative.

Alkylation of 2,3-dimethylcyclohex-2-enone[3] (II) with 1,5-di-iodo-3-methylpentane[4] in liquid ammonia using sodium amide as base gave the iodoketone (III; 35% yield) as a diastereomeric mixture. Bromination of (III) with *N*-bromosuccinimide (2 equiv) in carbon tetrachloride resulted in the formation of the bromo-dienone (IVa; 64% yield). Treatment of the bromo-ketone with chromous chloride resulted in reductive debromination and concurrent deconjugation, giving the ketone (V). The latter isomerised readily to the conjugated ketone (IVb; 79% yield from IVa) on heating in ethanol with toluene-*p*-sulphonic acid, or on attempted purification using silica gel or neutral alumina chromatography. The iodine atom of (IVb) was replaced on treatment with ethanolic dimethylamine at room temperature, yielding the amino-ketone (IVc; 63% overall yield from IVa). The amino-ketone was oxidised with hydrogen peroxide in methanol, and the resulting *N*-oxide (IVd), without purification, was pyrolysed at 430° under helium in a g.l.c. apparatus. A pyrolysis product corresponding to the largest peak in the gas-chromatogram was collected and further purified by preparative t.l.c. The compound obtained was the unsaturated ketone (VI).† Hydrogenation of (VI) afforded a saturated ketone, which was shown to be identical with norseychellanone (Ib) by i.r. and n.m.r. Transformation of the norseychellanone into racemic seychellene has been reported.[2]

All compounds described had the expected spectroscopic properties.

We thank Professors G. Ourisson and E. Piers for the identification of norseychellanone.

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† Other volatile pyrolysis products are now being investigated.

[1] G. Wolff and G. Ourisson, *Tetrahedron Letters*, 1968, 3849; *Tetrahedron*, 1969, **25**, 4903. See also N. Tsubaki, N. Nishimura, and Y. Hirose, *Bull. Chem. Soc. Japan*, 1967, **40**, 597.

[2] E. Piers, R. W. Britton, and W. de Waal, *Chem. Comm.*, 1969, 1069; K. J. Schmalzl and R. N. Mirrington, *Tetrahedron Letters*, 1970, 3219.

[3] L. I. Smith and G. F. Rouault, *J. Amer. Chem. Soc.*, 1943, **65**, 631.

[4] C. Cope and D. M. Gale, *J. Amer. Chem. Soc.*, 1963, **85**, 3743.