A New Approach towards the Synthesis of the Bicyclo[2,1,1]hex-2-ene System

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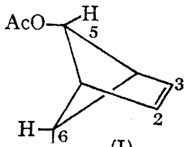
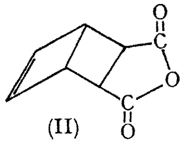
THREE reported syntheses of bicyclo[2,1,1]hex-2-enes have recently been described.[1] We now report an efficient synthesis of *exo*-bicyclo[2,1,1]hex-2-en-5-ol acetate (I).

Hydroboration of bicyclo[2,2,0]hexenedicarboxylic acid anhydride (II)[2] at −15°, followed by treatment with alkaline hydrogen peroxide, acetic anhydride, and finally boiling water, gave an acetoxydicarboxylic acid (III), m.p. 182—183·5°,† (60—70%). Oxidative bis-decarboxylation of (III) with lead tetra-acetate proceeded normally to give acetoxybicyclo[2,2,0]hexene (IVa) (*ca.* 40%), which was converted, *via* the hydroxy-derivative ($LiAlH_4$), into the corresponding *p*-nitrobenzenesulphonate (IVb), m.p. 73—74°, n.m.r., τ 1·65 (q, 4H), 3·56 (t, 1H), 3·79 (t, 1H), 5·17 (t, 1H) 6·55 (m, 2H), and 7·78 (t, 2H).

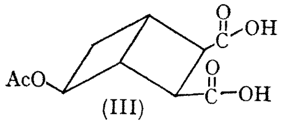
In acetic acid containing sodium acetate (2 equiv.), (IVb) solvolyzed with liberation of the theoretical amount of *p*-nitrobenzene-sulphonic acid (first-order rate constant, $k = 6{\cdot}07 \times 10^{-5}$ sec.$^{-1}$ at 89·7°). When the solvolysis was quenched at 50% completion, the product mixture contained starting material (IVb) (50%), benzene (5%), a new compound (I) (32%), an unidentified acetate (V) (11%), and minor products (2%).‡ Recycling of recovered (IVb) for a further solvolysis provided (I) in approximately 50% combined yield. Compound (I) was unstable under the solvolytic conditions and after eight half-lives of (IVb), the major product (more than 90% yield) was (V), indicating that (I) was converted into (V) under these acetolysis conditions.



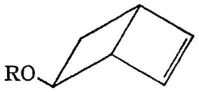
(I)



(II)



(III)



(IVa)R=Ac
(IVb)R=p-$NO_2 \cdot C_6H_4 \cdot SO_2$

A 100 Hz n.m.r. spectrum (CCl_4) of (I) showed τ 3·27 (t 2-,3-H), 5·31 (d, *J* 6·6, 5-H), 6·76 (m, 6-*exo*-H), 7·42 (q 1-,4-H), 7·72 (dd, *J* 6·6 and 5·7, 6-*endo*-H), and 7·98 (s, acetate). This spectrum and decoupling experiments displayed all the splitting patterns characteristic of bicyclo-[2,1,1]-hexene and -hexane derivatives, in particular, the

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† The corresponding *p*-nitrobenzenesulphonate dimethyl ester, m.p. 115—116°, underwent the base-catalyzed elimination to afford dimethyl tricyclo[3,1,0,0^{3,6}]hexane-1,2-dicarboxylate which was further transformed into 5-methoxybicyclo[2,1,1]hexane-2,3-dicarboxylic acid, m.p. 118°.

‡ The yields are not corrected for the sensitivity of the flame detector of the g.l.p.c.

long-range coupling between 5-*endo*-H and 6-*endo*-H and a unique geminal coupling-constant between 6-*endo*- and *exo*-protons.[3] Catalytic hydrogenation of (I) (Pt in MeOH) provided the corresponding dihydro-compound which was identical with an authentic specimen of *exo*-bicyclo[2,1,1]-hexan-5-ol acetate.[4] These results establish that the structure and stereochemistry of (I) are as shown.

A CH_2Cl_2 solution of (I) was transferred into fluorosulphuric acid at liquid-nitrogen temperature in a vacuum system. Upon mixing at $-60°$, the lower layer (FSO_3H) immediately became bright orange,[5] and showed the following n.m.r. spectrum (relative to internal CH_2Cl_2): τ 3·35 (ill-resolved d, 2H), 5·60 (ill-resolved d, 2H), 6·80 (dt, 1H), 7·30 (overlap of d and s, 1H and 3H) and 8·24 (dd, 1H). Irradiation either at signal τ 6·80 or 7·30 collapsed the signals at τ 8·24 to a doublet.

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