Tetrahedron Letters No. 6, pp 565 - 568.
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0040-4039/79/0201-0565$02.00/0

A NEW SYNTHESIS OF A HYDROAZULENONE

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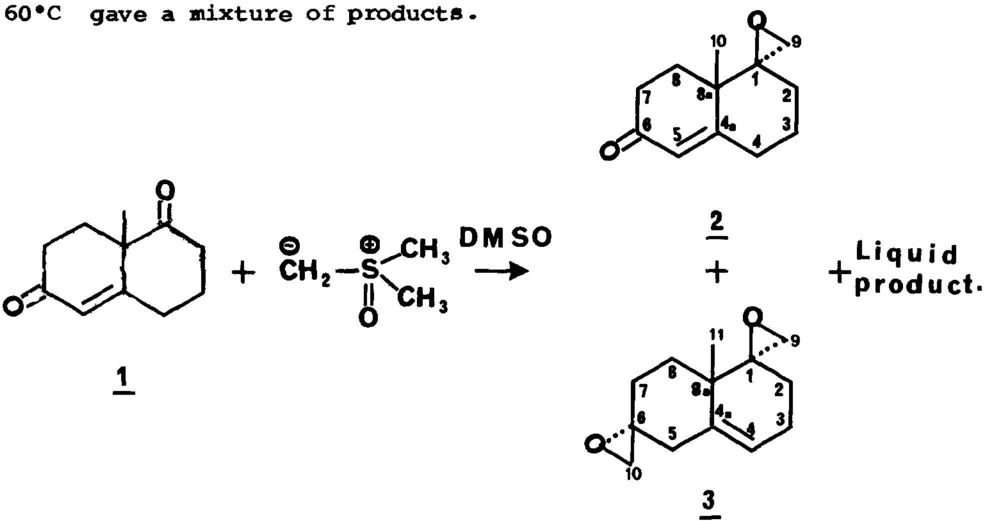
In recent years several approaches to hydroazulenes involving efficient and ingenious synthetic designs have been developed.[1] We report here a new route to 6-methyl-bicyclo(5,3,0)-deca-1,6-dien-3-one (4).[2]

Treatment of the bicyclic enedione (1) with dimethyloxosulfonium methylide (DMSM)[3] in dimethyl sulfoxide at 25°C followed by heating at 60°C gave a mixture of products.

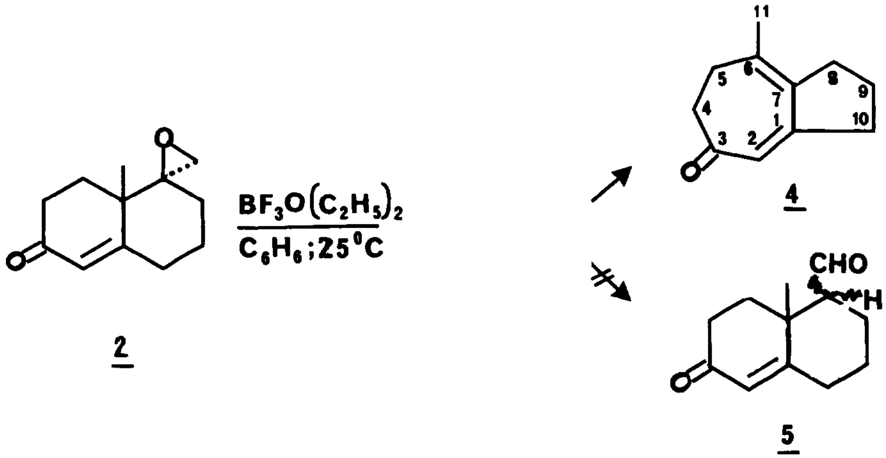


Chromatography over silica gel afforded spiro-1β-oxiranyl-6-oxo-8aβ-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene (2) as the major product. This compound,[4] mp.60-62°C (40%) $C_{12}H_{16}O_2$ (M^+ 192), had IR absorptions, at 1675 and 1623 cm^{-1} as well as UV absorption at λ_{max}^{EtOH} 236 nm (ϵ = 16470), which attest to the presence of a conjugated carbonyl function.

The oxirane methylene of the spiro epoxide generates peaks at δ 2.77, 2.43 (AB pair of doublets, J = 5.5 Hz, 2H) in ^{1}H NMR as well as at δ 48.9(t) in ^{13}C NMR spectra. The axial methyl group[5] at C-8a in (1) can be expected to direct the ylide to approach from the least hindered axial side.[6] DMSM is generally known to attack the carbonyl groups from the less hindered side.[7]

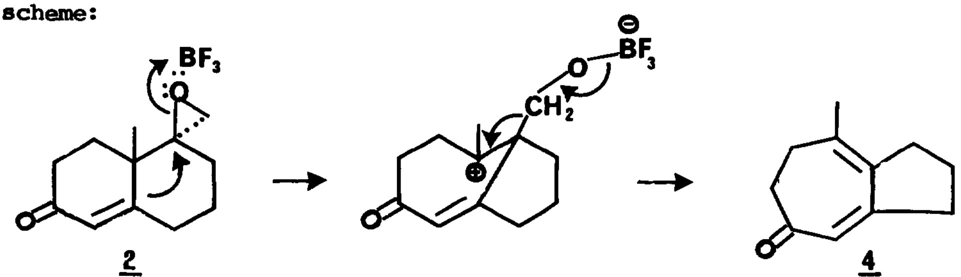
In addition to (2), a second product spiro-1β-oxiranyl-6α-oxiranyl-8aβ-methyl-1,2,3,5,6,7,8,8a-octahydronaphthalene (3) was also obtained in 5% yield. This compound,[4] mp.78-79°C $C_{13}H_{18}O_2$ (M^+ 206) showed absence of carbonyl absorption in IR and had only end absorption in UV λ_{max}^{EtOH} 206 nm (ϵ = 1176). ^{1}H NMR ($CDCl_3$): δ 5.45 (broad multiplet, 1H); 2.60,2.30 (AB pair of doublets, J = 5.5 Hz, 2H); 2.40 (s, 2H); 1.2-3.0 (m, 10H); 1.1 (s, 3H) ^{13}C NMR (20 MHz, $CDCl_3$): δ 138.5 s (C-4a); 122.2 d (C-4); 62.4 s (C-1); 58.5 s (C-6); 52.7 t (C-10); 49.7 t (C-9); 36.9 s (C-8a); 22.1 q (C-11). In addition, the off-resonance decoupled CMR spectrum showed five CH_2's at δ 39.1, 28.4, 28.1, 27.8 and 22.4. The assigned stereochemistry of the oxirane function at C-6 is consistent with the reported exclusive formation of α-oxiranes in the reaction of 3-keto steroids with DMSM.[8] The third product (ca. 10%) is currently being investigated.

Treatment of the spiro epoxide (2) with borontrifluoride etherate in benzene at 25°C resulted in the exclusive formation of 6-methyl bicyclo-(5,3,0)-deca-1,6-dien-3-one (4) instead of the expected bicyclic carboxaldehyde (5).



The hydroazulenone[4] (4) $C_{11}H_{14}O$ (M^+ 162) obtained pure as a yellow oil quite stable for over a month,[2] showed IR absorptions at 1665, 1630, 1595 cm^{-1}, UV λ_{max}^{EtOH} 303 nm (ϵ = 16190); 240 nm (sh, ϵ = 6601); ^1H NMR ($CDCl_3$): δ 5.65 (s, 1H); 2.50-2.00 (m, 8H); 1.80 (s, 3H). In addition a 2H quintet for the central CH_2 group in the five-membered ring appeared under the methyl signal. ^{13}C NMR (20 MHz, $CDCl_3$): δ 199.8 s (C-3); 156.9 s (C-1); 141.3 s (C-6); 126.3 s (C-7); 121.6 d (C-2); 20.3 q (C-11). The five CH_2's appeared as triplets between 20-37 ppm in the off-resonance decoupled spectrum.

The transformation of (2) to (4) can be rationalized by the following scheme:



This facile rearrangement would require the migrating bond to be trans and coplanar to the leaving group. Similar transformation involving epimeric spiroepoxides in polycyclic system has led to a mixture of aldehyde and rearranged olefin.[9] The exclusive formation of the rearranged product (4), in our case can be attributed to the favourable relative orientations of the migrating bond and the leaving group. This provides additional support to the assigned stereochemistry at C-1 in (2).

Further exploitation of this transformation as a versatile approach to hydroazulenic sesquiterpenes is under study.

Acknowledgements

The authors are grateful to Dr. K. Nagarajan, CIBA Research Centre, Bombay for analysis and mass spectral data and also to Dr. J. N. Shoolery, NMR Applications Laboratory, Palo Alto, California, for having provided us with ^{13}C spectral data reported here. GP is indebted to the Council of Scientific and Industrial Research for a Junior Research Fellowship.

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(Received in UK 7 December 1978)