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THE PERACID OXIDATION OF AN ALKENYLIDENECYCLOPROPANE[1a]

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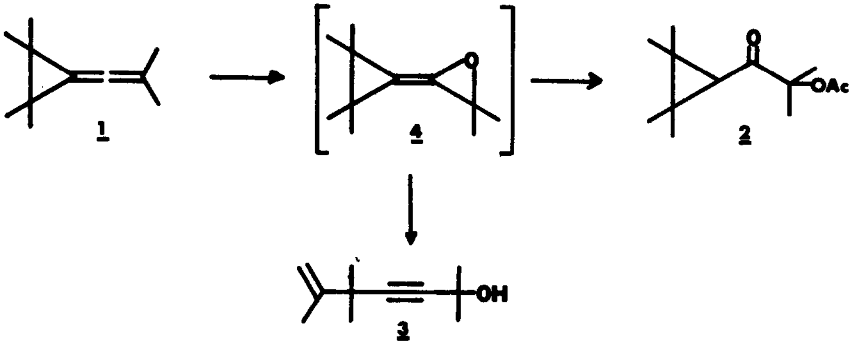
Our interest in allene oxides[2] and oxaspiropentanes[3] has prompted an investigation of the epoxidation of the fully methylated alkenylidenecyclopropane[4] 1, a potential precursor of one or both of these intreguing functional moieties. Oxidation was performed with one equivalent of peracetic acid in cold methylene chloride solution containing suspended sodium carbonate as an acetic acid scavenger[5]. This treatment afforded two major products and a third unidentified minor component (9%).

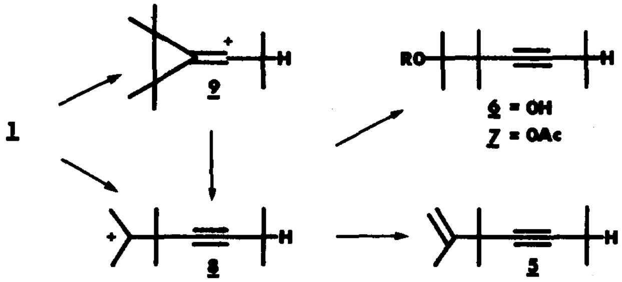
The predominant material (64%) was a crystalline solid, mp 44-44.5°, identified as cyclopropyl ketone 2 on the basis of spectroscopic data[6] and chemical precedent[2]. The infrared spectrum of 2 displays carbonyl absorption (5.77, 5.90 μ) appropriate for acetate and cyclopropyl ketone[7] functions, whereas the nmr spectrum evidences three different pairs of identical methyl groups on quaternary carbon (τ 8.83, 8.81, 8.59), an acetate methyl (τ 7.95), and a one-proton singlet at relatively high field (τ 8.48). The second important product (27%) was found to be 2,5,5,6-tetramethylhept-3-yn-6-en-2-ol (3). Its infrared spectrum indicates hydroxyl (2.9 μ) and disubstituted terminal methylene signals (3.21, 6.19, and 11.2 μ), while the nmr shows two unsplit six-proton methyl resonances (τ 8.72, 8.55), an olefinic methyl (τ 8.18), and typical terminal methylene multiplets (τ 5.30, 5.05). The clear definition of an otherwise transparent acetylene group in the form of intense absorption at 4.48 μ in the Raman spectrum[8] and the lack of a conjugated vinylacetylene chromophore[9] in the ultraviolet unambiguously secure structure 3.

The most straightforward description of these facts utilizes the allene oxide intermediate 4 derived from selective attack of peracid at the allene double bond remote from the cyclopropyl ring. The addition of acetic acid to 4 yields 2 *via* its enol. Alternatively, protonated 4 can fragment with cleavage of both epoxide and cyclopropyl rings to establish the acetylenic function in the open-chain, cationic precursor to 3.

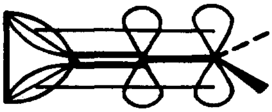


For comparison, the acid-catalyzed reaction of 1 was examined in an acetic acid-sulfuric acid mixture. The three products, formed in the ratio of 27:36:37, were identified as 2,3,3,6-tetramethylhept-4-yn-1-ene (5) [ir: 6.05 and 11.1 μ, $C{=}CH_2$; nmr: τ 8.85 (d, 6, J = 6.4 Hz) and 7.50 (septet, 1, J = 6.4 Hz) $CH(CH_3)_2$, 8.72 (s, 6) $C(CH_3)_2$, and 8.18 (bs, 3), 5.32 (m, 1), 5.05 (m, 1) $C(CH_3){=}CH_2$; uv (hexane): λ_{max} 228 nm (ε 157)], 2,3,3,6-tetramethylhept-4-yn-2-ol (6) [ir: 2.9 μ; Raman: 4.49 μ $C{\equiv}C$; nmr: τ 8.85 (d, 6, J = 6.6 Hz), 8.84 (s, 6), 8.80 (s, 6), 7.48 (septet, 1, J = 6.6 Hz), and 8.13 (s, 1)], and the corresponding acetate 7 [ir: 5.75 μ; nmr: τ 8.84 (d, 6, J = 7.0 Hz), 8.78 (s, 6), 8.41 (s, 6), 8.06 (s, 3) OAc, and 7.49 (septet, 1, J = 7.0 Hz). These compounds were interrelated by the clean 400° pyrolysis of 7 to give 5 and by lithium aluminum hydride cleavage of the acetate group of 7 to yield 6.

Electrophilic attack on 1 by a proton is apparently also specific for the olefinic unit away from the cyclopropyl ring. Furthermore only open-chain compounds are found in this instance. These products have as their immediate precursor the acetylenic cation 8 which is best seen as arising from the vinyl cation 9, although this latter species could actually be bypassed in a concerted transformation of 1 to 8.



Some understanding of the specificity of electrophilic attack and of the facile formation of open-chain acetylenic products can be achieved by consideration of the special spatial relationship of the cyclopropyl ring and the remote double bond. Atomic orbital representation 10 illustrates the overlap of the cyclopropyl σ-bonds with the π-orbital of the reactive olefinic unit which is rigidly enforced by the allene geometry. An important consequence of this feature of 10 is the ability of the cyclopropyl system, with its well-known propensity for stabilizing cationic centers[10], to participate favorably in the transition state for electrophilic attack at this double bond without appreciable change of molecular geometry. This process is thereby promoted relative to its competitors.[11] As indicated above it is not clear that vinyl cation 9 is a true intermediate in the attack of a proton on 1, since the orbital system is perfectly arranged for synchronous fission to 8, a process potentially favored by substantial relief of bond-angle strain. It is, furthermore, possible that allene oxide 4 does not intervene in the formation of acetylenic alcohol 3 in the epoxidation reaction, but we view a concerted process as less likely in this case.



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