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A DIANIONIC OXY-COPE REARRANGEMENT ROUTE TO BENZOTROPONES - PART XII

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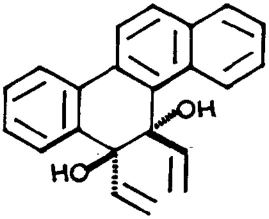
Abstract : The divinyl carbinols 3 and 6 furnished the benzotropones 4 and 7 respectively, when treated with base.

Oxy-Cope rearrangements of divinyl carbinols have been well documented(1,2). We report here the synthesis and base catalysed rearrangement of the divinyl carbinols 3 and 6 (3).



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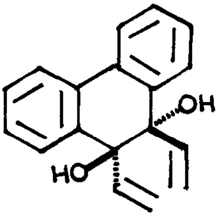

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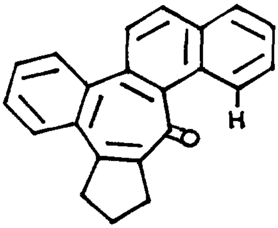
5,6-chrysenequinone 1 (4) was diethynylated (5,6) with sodium acetylide in liquid ammonia to give 5,6-diethynyl,5,6-dihydrochrysene-5,6-diol 2 as a colourless crystalline solid**, m.p. 196-198°C (40%). Partial hydrogenation of the carbinol 2 in the presence of Pd-$CaCO_3$ in pyridine furnished the divinyl carbinol 3 as a crystalline solid, m.p. 132-134°C in 50% yield. The carbinols 2 and 3 exhibited satisfactory spectral characteristics (IR and NMR). Based on analogy (5) the carbinols 2 and 3 have been assigned the trans stereochemistry.

Treatment of the vinyl carbinol 3 with two equivalents of KH in THF (7) at reflux temperature for 12 hr yielded after workup 14-oxo-1,2,3,14-tetrahydro-benzo(e)naphth(2,1-g)azulene 4 and not 5 which can arise by an alternate transannular reaction followed by dehydration. Compound 4 was obtained as a crystalline solid, m.p. 217-219°C (40%). UV : $\lambda_{max}^{CHCl_3}$ 247 (ϵ = 43,440), 290 (ϵ = 25,910) and 338 nm (sh, ϵ = 3811); IR(KBr): 2930 (-CH), 1635 ($>$C=O) and 1600 cm^{-1} (-C=C-); NMR ($CDCl_3$/TMS) : δ 2.0 (quintet, 2H, J = 7 Hz), 3.05, 3.15 (two overlapping triplets, 4H, J = 7 Hz), 7.4-8.1 (m, 9H, aromatic protons) and 8.6 (m, 1H, peri proton of naphthalene); Mass spectrum (m/e-296) and elemental analysis showed a molecular formula of $C_{22}H_{16}O$. Evidence in favour of structure 4 was obtained by comparison with the benzotropone 7 obtained by rearrangement[8] of the vinyl carbinol 6 (3) with two equivalents of KH in refluxing THF for 24 hr.



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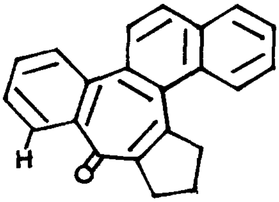

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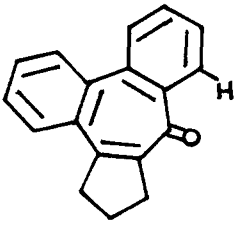

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12-oxo-1,2,3,12-tetrahydro-dibenz(e,g)azulene 7 was obtained as a crystalline solid, m.p. 127-129°C (5%). UV : λ_{max}^{EtOH} 241 (ϵ = 22,750), 264 (ϵ = 22,360) and 319 nm (ϵ = 2354); IR (KBr) : 2940 (-CH), 1630 ($>$C=O) and 1595 cm^{-1} (-C=C-); NMR (CDCl$_3$/TMS) : δ 1.95 (quintet, 2H, J = 7 Hz), 3.05, 3.15 (two overlapping triplets, 4H, J = 7 Hz), 7.4-8.1 (m, 8H, aromatic protons). Mass spectrum (m/e-246) and elemental analysis showed a molecular formula of $C_{18}H_{14}O$.

The rearrangement product obtained from the vinyl carbinol 3 showed a low field proton at δ 8.6 when compared to the tropone 7. This difference can be accounted for by only structure 4 which has a peri hydrogen on the naphthalene ring proximate to a carbonyl group(9). The formation of compound 4 can be rationalized on the basis of an initial (3,3) sigmatropic rearrangement of the dianion, followed by a transannular reaction and dehydration of the intermediate aldol. In the case of both the carbinols 3 and 6 the trans divinyl moieties must be dipseudo-equatorial for the rearrangement to occur. The above transformations involving an anionic oxy-Cope followed by a transannular reaction provide a facile entry into substituted benzotropones.

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8. Surprisingly, a better yield (25%) of the tropone 7 was obtained by an oxy-Cope rearrangement of the neutral substrate 6 (Δ, 200°C for 40 hr in cyclohexane).
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** All new compounds gave satisfactory elemental analysis.

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