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THE TRICYCLO[5.2.0.0^{2,5}]NONANE SYSTEM: A SYNTHESIS OF HOMOCUBANONE[1]

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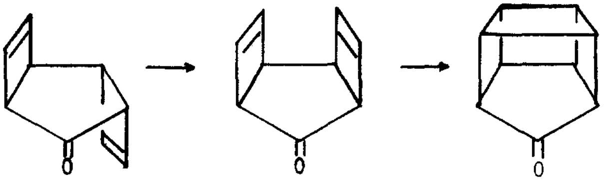
Elegant syntheses of cubanes,[2] homocubanes,[3] and bishomocubanes[4] have been reported; however, the overall yields of these syntheses are relatively low. We considered the possibility that photochemical ring closure in ketone **1** would lead to homocubanone, **2**, in good yield. We report here an efficient synthesis of <u>anti</u>-tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-one, **3**, and its photoisomerization to homocubanone.

Irradiation of 2-cyclopentenone with an excess of 1,2-dichloroethylene provided a stereoisomeric mixture of adducts **4**[5] in 92% yield. Dehydrogenation of **4** with selenium dioxide in <u>t</u>-butanol[6] yielded the cyclopentenones **5** (51%), λ_{max}^{EtOH} 229 nm (ε 3700), $\nu_{max}^{CCl_4}$ 1720 cm^{-1}. Photocycloaddition of **5** with dichloroethylene (as above) provided the tricyclic tetrachloroketones **6**. Conversion of **6** into the ethylene ketals, dehalogenation using sodium in liquid ammonia, and hydrolysis of the ketal with 1.5M hydrochloric acid gave the <u>anti</u>-dienone **3**, bp 34°, 0.5 torr, in 46% yield from **5**. Ketone **3** has λ_{max}^{EtOH} 306 nm (ε 267), $\nu_{max}^{CCl_4}$ 1725 cm^{-1}, and δ_{CCl_4} 6.07 (AB quartet ΔAB 7.5Hz, J 2.7Hz; each peak of the upfield doublet is further split into a doublet J 1.3Hz by coupling with one of the bridgehead protons). Anal. Calc'd for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.73; H, 6.14.

That the dienone obtained above is the <u>anti</u>-isomer **3** and not **1** was shown by reduction with lithium aluminum hydride to give the unsymmetrical alcohol **7**. In alcohol **7** the two nonequivalent cyclobutene rings should give rise to two AB quartets whereas each of the two alcohols derived from **1** is symmetrical and a single AB quartet is expected from each. The reduction, in fact, gave a single (glpc) crystalline alcohol, mp 49.5-50.8°. The nmr spectrum determined in carbon tetrachloride containing pyridine exhibits two two-proton AB quartets δ 5.98 (ΔAB 21.1Hz, J 2.6Hz) and 5.95 (ΔAB 5.3Hz, J 2.8Hz); the <u>anti</u> stereochemistry is established.

Irradiation of 3 (570 mg in 200 ml of methylene chloride) with ten 15 watt "blacklights" for 30 hr gave after solvent removal and short-path distillation 390 mg (68.4%) of homocubanone, 2, which was identified by comparison of ir and nmr spectra with those of authentic material.[7] The formation of homocubanone from 3 surely involves as an intermediate the syn-dienone 1, which could arise from 3 via the now familiar 1,3-acyl shift common to β,γ-unsaturated ketones.[8] The final ring closure probably occurs via intramolecular triplet energy transfer from carbonyl to olefin followed by cycloaddition of the olefin triplet with the adjacent double bond. No evidence which rules out any other process leading from 3 to 2 has been obtained, however.[9]

This seven-step synthesis of homocubanone in overall yield of 14% may be modified to provide a variety of substituted homocubane derivatives.



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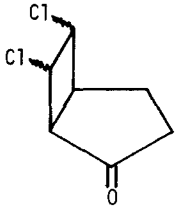

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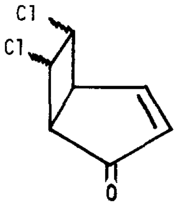

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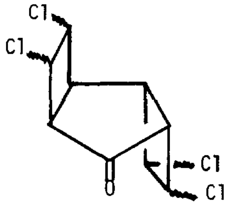

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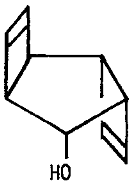

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