

The following paper was originally published in HETEROCYCLES, 1973, 1, 39. Unfortunately, errors in the text were such as to render the paper unintelligible. We are therefore reproducing the whole paper with revised text.

SELECTIVE REDUCTION OF 12-OXA[4.4.3]PROPELLA-2,4,7,9-TETRAENE
CATALYZED BY AN ARENECHROMIUM TRICARBONYL

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Hydrogenation of the title compound afforded chiefly 1,4-addition of hydrogen from the "top" face of each cyclohexadiene ring.

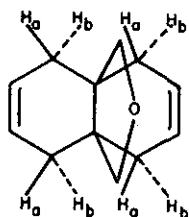
Since the heterocyclic propellane 1 contains conjugated dienes in two of its rings, it is a good substrate for investigating the course of hydrogen addition when arenechromium tricarbonyls are used as homogeneous catalysts in the hydrogenation of bicyclic and tricyclic systems.¹ Further, it was of interest to investigate if each ring behaved independently of the other² and whether the hydrogen atoms would be delivered to both diene systems from "above" or from "below" (see arrows in 1a), or from either direction.



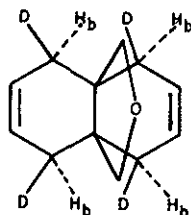
In a typical experiment 1 (78 mg; ca. 0.4 mmol) was reduced in cyclohexane (50 ml) solution in the presence of phenanthrene-Cr(CO)₃ (157 mg) at 500 psi and 150°. Reduction was complete after 6 hr. The reaction mixture contained the symmetrical diene 2 (77%) and the unsymmetrical diene 3 (23%; by glc). Purification by preparative glc (6' x 1/4" column packed with 15% DEGS) permitted the isolation of 2 in 96% purity and 3 in 90% purity (by glc and nmr). The purest sample of 3 still contained (by glc) 6.5% of 2 and 3.5% of an unknown which is presumed to be one or both of the

other possible unconjugated dienes (one double bond in each ring). Further reduction to a mono-olefin or to the perhydro-compound did not occur. The latter compounds are known in this laboratory³ and were not observed during isolation by glc, nor were their corresponding mass peaks observed. The purest sample of 3 had b.p. 50° (0.1 mm), 59-60° (0.3 mm). (Found: C, 81.77; H, 9.15; M.W. 176. C₁₂H₁₆O requires C, 81.24; H, 8.83%; M.W. 176.25).

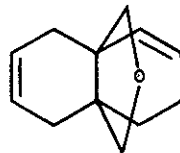
The structure of 3 was inferred from its nmr spectrum. It exhibited absorption (CDCl₃, τ) at 4.32-4.52 (m, 4 vinylic H); 6.25 (s, 4 CH₂O); 7.93 (br d, J = 3Hz, 6 allylic H); 8.17-8.75 (m, 2 CH₂).



2



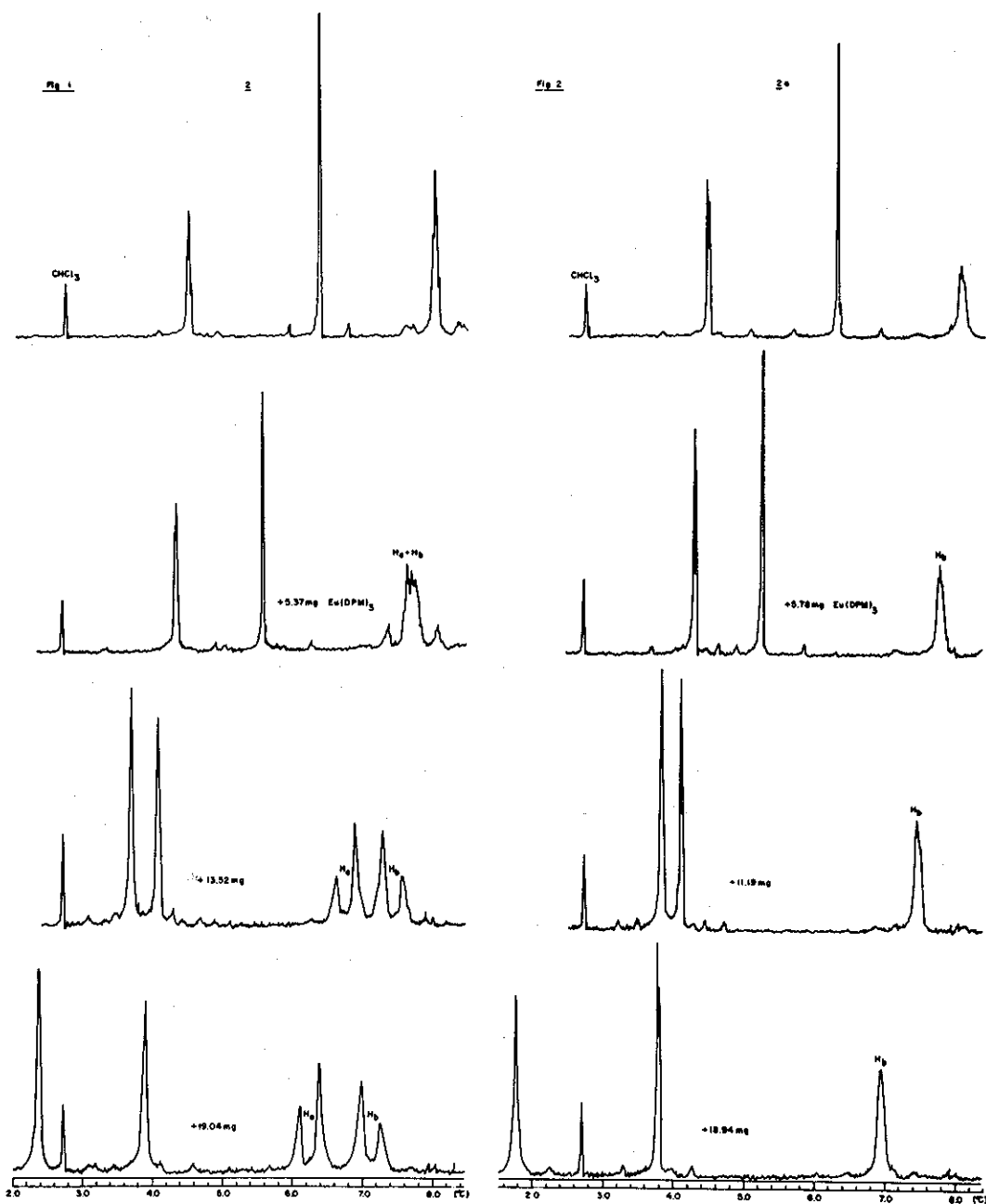
2a

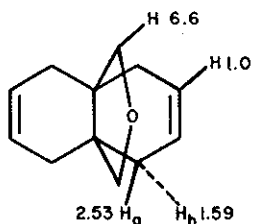


3

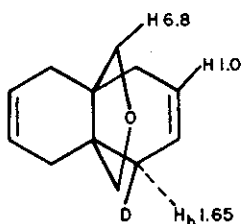
Further, the direction of attack of 1 by hydrogen could be inferred from reduction using deuterium in the presence of the same catalyst.

Observation of models of 2 shows that no matter what conformation obtains in each cyclohexene ring, all of the allylic protons marked H_a in formula 2 are closer to the ether oxygen atom than those marked H_b. Thus, we have a means, using a lanthanide shift reagent, for observing H_a and H_b at different concentrations of the shift reagent in the undeuterated 2 and in the deuterated analog 2a. Fig. 1 shows the nmr spectra of 2 and Fig. 2 shows the corresponding spectra for 2a. The relative slopes of the straight lines obtained by plotting $\delta\Delta\nu$ vs the concentration of [Eu(DPM)₃] / [Diene] are recorded for the various protons in the following formulae for 2 and 2a.

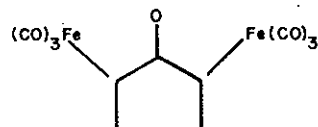




2



2a



4

It may therefore be unequivocally deduced that deuterium (and therefore hydrogen in the analogous reduction of 1 by hydrogen) is delivered from the top face of each cyclohexadiene ring.

This is reminiscent of the formation of 4 alone (amongst 3 possible bis-Fe(CO)₃ complexes) by treating 1 with Fe(CO)₅. If this result is explained by the metal carbonyl first coordinating with the ether oxygen of 1, one may invoke a similar initial coordination with the hydrogenation catalyst which permits the delivery of hydrogen or deuterium to the top face of 1.

In the Diels-Alder reaction of 1 with 4-phenyl-1,2,4-triazoline-3,5-dione,² the first mole of dienophile attacks the bottom face but this is not comparable to the above cases as there is no reason to expect analogous coordination of the dienophile with the ether oxygen.

REFERENCES

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3. J. Altman, E. Babad, J. Itzhaki and D. Ginsburg, Tetrahedron, Suppl. 8, Part I, 279 (1966).

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