Tetrahedron Letters No. 12, pp 993 - 996, 1975. Pergamon Press. Printed in Great Britain.

THE ADDITION OF DIFLUOROCARBENE TO 10-METHYL-Δ^8-2-OCTALONE 2-ETHYLENE ACETAL; X-RAY CRYSTAL STRUCTURE OF 8β,9β-DIFLUOROMETHYLENE-10-METHYL-2-DECALONE 2-ETHYLENE ACETAL

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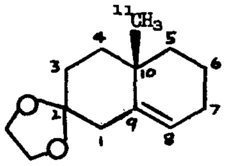
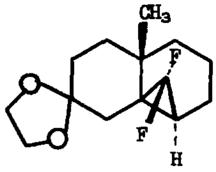
(Received in USA 27 December 1974; received in UK for publication 11 February 1975)

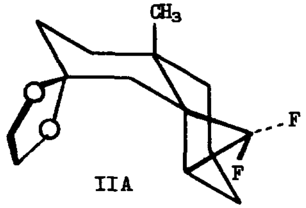
We recently reported that the addition of CF_2 to 10-methyl-Δ^8-2-octalone 2-ethylene acetal (I) afforded, in 68% yield, two isomeric adducts with a distribution of 250:1.[3] The major product was assigned the β-difluoromethylene stereochemistry (II) on the basis of (1) analogy to β CF_2 additions to Δ^5 steroidal olefins[4] and to the β-endo-F addition of CFCl to I[5], supported by a 0.6 Hz. long-range coupling[4,6-8] of F and CH_3 observed in the pmr spectrum of the product (II, exo-F=Cl); (2) similarity of the angular methyl chemical shifts of the latter[5] and of II; and (3) calculations[9] of δ values for the angular methyl resonances of II and its α-difluoromethylene isomer, which indicated that II should have the higher field resonance.[3]



I



II



IIA

The absence of observable long-range coupling between the β-endo-F atom and angular methyl group of II[3] was disturbing, however, particularly in view of the common occurrence of such coupling in steroidal analogs.[4] Because the overwhelming stereoselectivity exhibited by CF_2 in its addition to I has important mechanistic and synthetic implications,[3-5] it was crucial to definitively establish the stereochemistry of CF_2 addition. Accordingly, II was prepared from I and excess $C_6H_5HgCF_3$/NaI, refluxed in benzene for 5 days.[3] Single crystals of II were obtained from the crude product by distillation, followed by sublimation (mp, 51-53°), and a crystal was subjected to X-ray analysis with an Enraf Nonius CAD-3 diffractometer (CuKα radiation).

Crystals of II are monoclinic, four molecules to a unit cell, with $a = 11.300(11)$, $b = 14.005(11)$, $c = 8.385(3)$ Å, and $\beta = 101.6(1)^0$. The space group is $P2_1/c$. The intensities of 1142 unique reflections with 2θ values up to 120^0 were measured, and the structure was solved by direct methods[10] on the basis of 441 |E| values above 1.0 . The structure was refined by full matrix least-squares methods, with anisotropic temperature factors for all the non-hydrogen atoms.[11,12] A final difference Fourier map, calculated at R = 10.3%, yielded the location of all

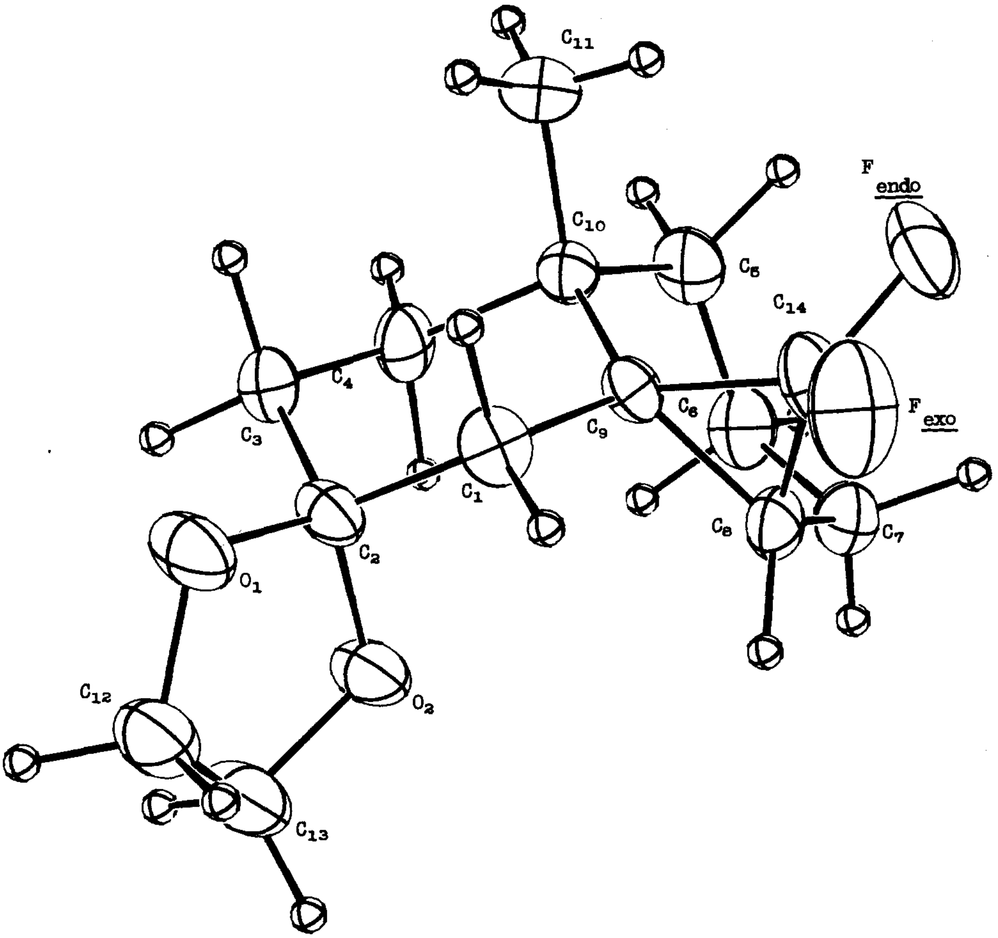


FIGURE 1. An ORTEP rendering of II (*c.f.*, IIA). The ring carbon atoms are numbered in accord with structure I, with the addition of the difluoromethylene carbon atom, C_{14}. Note the spatial relationship between the endo cyclopropyl fluorine atom, F_{endo}, and the angular methyl group, C_{11}.

20 H atoms. Further least-squares refinement, including the H atoms as a fixed atom contribution to the overall structure factor calculation, resulted in convergence with a final conventional R factor of 6.26%. An ORTEP drawing of the structure appears in Figure 1 (*cf.*, IIA).[13]

The X-ray analysis clearly establishes the *cis* A/B ring junction of II, and validates our previous stereochemical assignment.[3] Moreover, Figure 1 shows that II adopts the "nonsteroid" conformation, IIA, in which the β-*endo*-F atom and the angular methyl group are far apart. If II maintains this conformation in solution, then long-range $F\text{-}CH_3$ coupling is not expected. The "converging-vector rule" states: "long-range coupling between angular methyl protons and fluorine five or more σ-bonds apart may occur only when a vector directed along the C-F bond, and originating at the carbon atom, converges upon and intersects a vector drawn along an angular methyl C-H bond in the direction of the proton, and originating at the methyl carbon."[7] Examination of Dreiding Models and vector analysis (using the X-ray structure coordinates)[14] indicate that this situation *does not obtain* for II in the conformation (IIA) of Figure 1.

Our observations can therefore be construed as further support for both the (empirical) converging-vector rule,[4,6-8] and for the preference for the nonsteroid conformation in *cis*-10-methyl-2-decalone and its derivatives.[9,15-18]

Acknowledgments. We are grateful to Prof. H. J. Schugar and Dr. John Thich for making available the facilities of the Rutgers X-ray laboratory, and to Dr. Thich for assistance with the structure analysis. We thank the National Science Foundation and the National Institutes of Health for financial support. P. B. thanks the Rutgers School of Chemistry for a summer fellowship, sponsored by Exxon Research and Engineering Co.

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(1) Fellow of the Alfred P. Sloan Foundation.

(2) Henry Rutgers Fellow.

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(11) In addition to local programs for the IBM 360/67 computer, local modifications of the following programs were employed: Zalkin's FORDAP Fourier program; Johnson's ORTEP II thermal ellipsoid plotting program; Busing, Martin, and Levy's ORFEE error function and ORFLS least-squares programs.

(12) The analysis of variance was carried out using the program NANOVA, obtained from Dr. I. Bernal; see J. S. Ricci, Jr., C. A. Eggers, and I. Bernal, *Inorg. Chem. Acta*, **6**, 97 (1972).

(13) Additional details of the X-ray analysis, including tables of bond lengths and angles, will appear in the Henry Rutgers Thesis of P. Bekiarian, Rutgers University, New Brunswick, 1975, and in a publication by P. Bekiarian and J. Thich (to be submitted).

(14) We thank Professor T. Butler, Rutgers University Mathematics Department for help with this calculation.

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(16) D. R. Elliot, M. J. T. Robinson, and F. G. Riddel, *Tetrahedron Letters*, 1693 (1965).

(17) The presence of a 0.6 Hz. long-range F-CH_3 coupling in II (*exo*-F=Cl)[5] might indicate a slightly larger population of "steroid" conformer than in the case of II.

(18) A referee suggested that Fig. 1 be augmented by another ORTEP projection which would better depict the nonintersection of the C-H and C-F vectors. Our experience has been that two-dimensional projections are rather unsatisfactory for demonstrating this property of II, and that Fig. 1 is as good as several alternatives which we have tried. The best demonstrations employ Dreiding models, or vector analysis, as indicated in the text.