Tetrahedron Letters No. 36, pp 3401 - 3404.

0040-4039/79/0901-3401$02.00/0

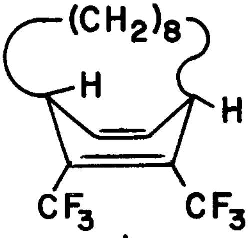
THE SYNTHESIS AND STRUCTURE OF 10,11-BISTRIFLUOROMETHYL-*i,o*-BICYCLO[7.2.2]TRIDECA-10,12-DIENE. A HIGHLY STRAINED INSIDE-OUTSIDE BICYCLOALKANE DERIVATIVE.

Paul G. Gassman*, Stewart R. Korn, Thomas F. Bailey, Thomas H. Johnson[1]
Department of Chemistry, University of Minnesota, Minneapolis, MN 55455

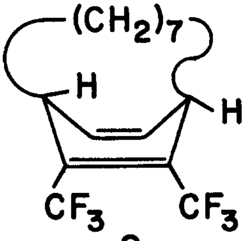
Janet Finer and Jon Clardy*[2]
Ames Laboratory-USERDA and Department of Chemistry, Iowa State University
Ames, Iowa 50011

10,11-Bistrifluoromethyl-*i,o*-bicyclo[7.2.2]trideca-10,12-diene has been prepared by the Diels-Alder addition of hexafluoro-2-butyne to *cis, trans*-cycloundeca-1,3-diene. Purification was accomplished via formation of an iron tricarbonyl complex whose structure was established via X-ray crystallography.

Relatively little is known about the chemistry of inside-outside bicyclic molecules. Of the few known examples[3-5] of such carbocyclic systems, only the *i,o*-bicyclo[8.2.2]tetradeca-11,13-diene derivatives showed behavior which could be associated with ring strain.[4-6] Because of the somewhat unusual chemical reactivity of **1**, we were intrigued with the possibility of preparing even more highly strained molecules with inverted bridgeheads. We now wish to report the synthesis of 10,11-bistrifluoromethyl-*i,o*-bicyclo[7.2.2]trideca-10,12-diene (**2**) and the conclusive establishment of the structure of its iron tricarbonyl complex by X-ray crystallography.



1

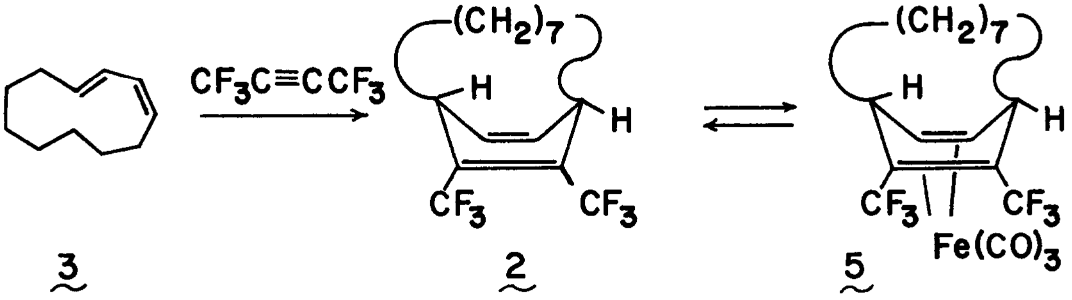


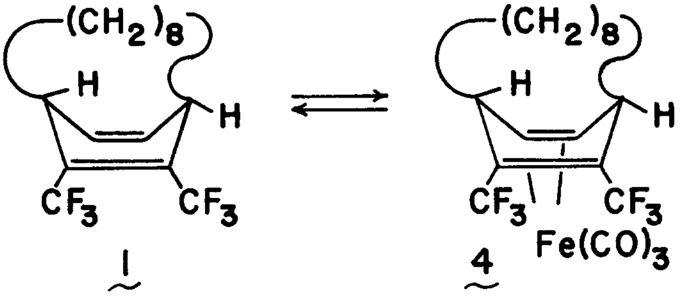
2

In principle, **2** should be able to be prepared by a procedure similar to that used for the preparation of **1**,[3] namely, a Diels-Alder reaction between hexafluoro-2-butyne and the appropriate diene, *cis*, *trans*-cycloundeca-1,3-diene (**3**). In practice this would require the synthesis of quantities of pure **3**, and the ability of the diene portion of **3** to exist in a cisoid configuration. The synthesis of *cis, trans*-cycloundeca-1,3-diene was accomplished by a combination of literature procedures.[7-9]

Treatment of **3** with a 50% excess of hexafluoro-2-butyne in a Carius tube at 175°C for 5 days gave a mixture of **3** (5%), **2** (76%),[10] and an unidentified component (*ca.* 19%). Numerous attempts to separate cleanly **2** and the unidentified component by physical methods (including various chromatographic techniques) were unsuccessful in our hands. Thus, we sought a chemical method of separation. Because of the more readily available nature of **1**, it was used as a model for 2. Treatment of 1 with excess diiron enneacarbonyl gave a 95% yield of the iron tricarbonyl complex, 4, mp 82-83°C.[11] Treatment of this complex with ceric ammonium nitrate regenerated 1 from 4 in 89% yield.

In order to utilize this process for the purification of 2, the crude reaction mixture from the reaction of 3 with hexafluoro-2-butyne was treated with a five fold excess of diiron enneacarbonyl in benzene under nitrogen at 25°C for 24 h. This process was repeated twice with 2.5 fold excesses of the diiron enneacarbonyl (total of 10 equivalents). Removal of the solvent below 40°C followed by chromatography of the residue gave 71% of 5 (based on 3) as yellow-orange crystals, mp 87-88°C.[12] The proton NMR spectrum of 5 was very similar to that of 4; ($CDCl_3$) δ 4.30 (1H, m), 4.04 (1H, m), 3.66 (1H, m), 3.58 (1H, m), and 2.50-1.25 (14H, m) Treatment of 5 with ceric ammonium nitrate gave an 88% yield of 2; n_D^{24} 1.4422; ^{1}H NMR ($CDCl_3$) δ 6.25 (1H, m), 6.02 (1H, m), 3.48 (1H, m), 2.92 (1H, m), 2.20-1.05 (14H, m). When pure 2 was treated with diiron enneacarbonyl, a 95% yield of 5 was obtained. Thus, the interconversion of 2 and 5 occurred without skeletal rearrangement.





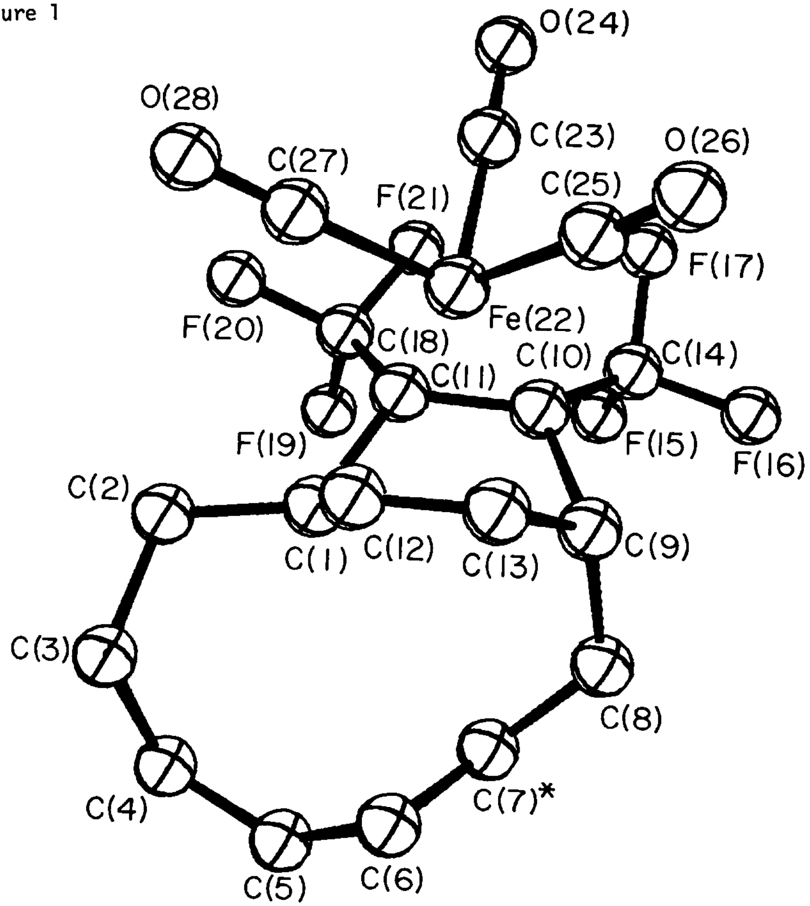
The structural assignment of 2 was based on the method of formation and by analogy of its preparation to the preparation of 1. The structural assignment of 1 was in turn based on chemical interconversions and on complex spectral data. Thus, it was felt that definitive evidence was needed for the structure of 2. In order to accomplish this goal an X-ray crystallographic study of 5 was undertaken.

Dark orange crystals of $C_{18}H_{18}O_3F_6Fe$ belonged to the centrosymmetric monoclinic space group $P2_1/c$. The measured cell constants, a=15.19(5)Å, b=8.390(2)Å, c=15.543(9)Å, and β=106.9(1)Å, gave a calculated density of 1.58 g/cc for four molecules in the unit cell. Data were collected on a fully-automated four-circle diffractometer using a ω-scan technique and Zr-filtered Mo radiation (λ=0.71069Å). After Lorentz-Polarization corrections, 2778 of the 3740 reflections (∿74%) with 2Θ ≤ 50° were considered observed ($F_0 \geq 3\sigma (F_0)$).

A combination of direct methods and Fourier syntheses was used to locate all non-hydrogen atoms.[13] The structure was disordered with C(7) appearing in two positions. An atom at each of these positions was included in the model. The initial occupancy of the disordered positions was set at 0.5 and then allowed to vary while the temperature factor was held fixed. All heavy atoms were refined anisotropically. In addition, all hydrogens save one were located and refined isotropically. Anomalous scattering factor corrections were made, and the final conventional R-factor for the structure was 0.088 for the observed reflections.

Figure 1 is a computer generated drawing of the molecule. The X-ray determination confirms the inside-outside nature of this bicyclic hydrocarbon. Bond distances and angles, when corrected for the large anisotropic thermal motion apparent in the biggest loop, generally agree well with accepted values.[14]

Figure 1



In summary, we have unequivocally established the inside-outside skeletal structure of **5** and (by extrapolation) of **2**. We are currently exploring the chemical and physical properties of this first example of an *i,o*-bicyclo[7.2.2]tridecadiene derivative.

ACKNOWLEDGEMENT. We are indebted to the National Science Foundation for a grant to P.G.G. which supported this investigation.

REFERENCES AND NOTES.

1. Stanwood-Johnston Memorial Fellow, 1976-1977.

2. Camille and Henry Dreyfus Teacher-Scholar Grant Awardee, 1972-1977. Current address - Department of Chemistry, Cornell University, Ithaca, New York 14853.

3. P.G. Gassman and R.P. Thummel, *J. Am. Chem. Soc.*, **94**, 7183 (1972); P.G. Gassman, S.R. Korn, and R.P. Thummel, *ibid.*, **96**, 6948 (1974).

4. C.H. Park and H.E. Simmons, *J. Am. Chem. Soc.*, **94**, 7184 (1972).

5. See also R.J. Sundberg and F.X. Smith, *J. Org. Chem.*, **40**, 2613 (1975); A.E. Kober and T.L. Westman, *ibid.*, **35**, 4161 (1970); J.G. Vinter and H.M.R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 5466 (1974).

6. P.G. Gassman and T.H. Johnson, *J. Am. Chem. Soc.*, **98**, 861 (1976).

7. W. Ziegenbein, *Chem. Ber.*, **94**, 2989 (1961).

8. R.W. Fawcett and J.O. Harris, *J. Chem. Soc.*, 2673 (1954).

9. In our hands, considerable modification of the literature procedures was required. Bromination of cyclododecanone in acetic acid gave 2,12-dibromocyclododecanone in 85% yield. Treatment of the dibromide with potassium hydroxide gave cycloundecene-1-carboxylic acid in 70% yield. Decarboxylation of this acid with copper in quinoline produced cycloundecene in 51% yield. The bromination of cycloundecene with N-bromosuccinimide in carbon tetrachloride gave a 69% yield of 3-bromocycloundecene. Dehydrobromination of this bromide with quinoline yielded 59% of **3**; $n_D^{24} = 1.5040$ (lit[8] $n_D^{25} = 1.5034$); $\lambda_{max}^{isooctane}$ 227 nm (ε 8550), $\lambda_{max}^{ethanol}$ 226 nm (ε 6215), [lit[8] $\lambda_{max}^{ethanol}$ 225 nm (ε 6160)].

10. Satisfactory elemental analyses and exact mass molecular weights were obtained on all new compounds.

11. ^{1}H NMR ($CDCl_3$) δ 4.21 (1H, m), 3.87 (1H, m), 3.81 (1H, m), 3.47 (1H, m), 2.50-1.19 (16H, m).

12. These complexes appeared to be slightly temperature sensitive. Removal of the solvent at higher temperatures resulted in slightly reduced yields and an accompanying decrease in purity. The yield and mp are of material that was recrystallized from hexane following chromatography on deactivated alumina.

13. The following library of crystallographic programs was used: G. Germain, P. Main and M.M. Woolfson, *Acta Cryst.*, **B24**, 274 (1970) and MULTAN, C.R. Hubbard, C.O. Quicksall, and R.A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFT and FRIEDEL," USAEC Report IS-2625, Iowa State University-Institute for Atomic Research, Ames, Iowa, 1971; W.R. Busing, K.O. Martin, and H.A. Levy, "A Fortran Crystallographic Least Squares Program," USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965; C. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program," U.S. Atomic Energy Commission Report ORNL-3794, Oak Ridge, Tenn., 1965.

14. A full discussion of the molecular geometry will be given in a full paper.

(Received in USA 18 April 1979)