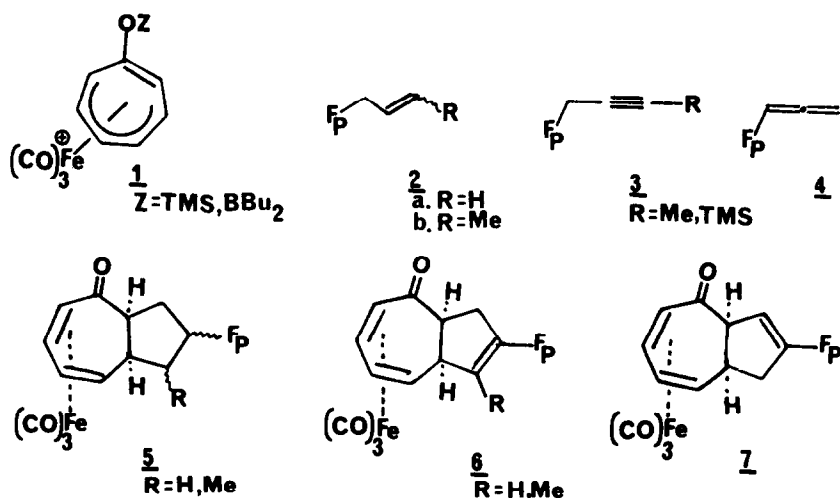


(3+2) Cyclopentane Annulation Reactions.
Hydroazulene Synthesis Using Organoiron Reagents

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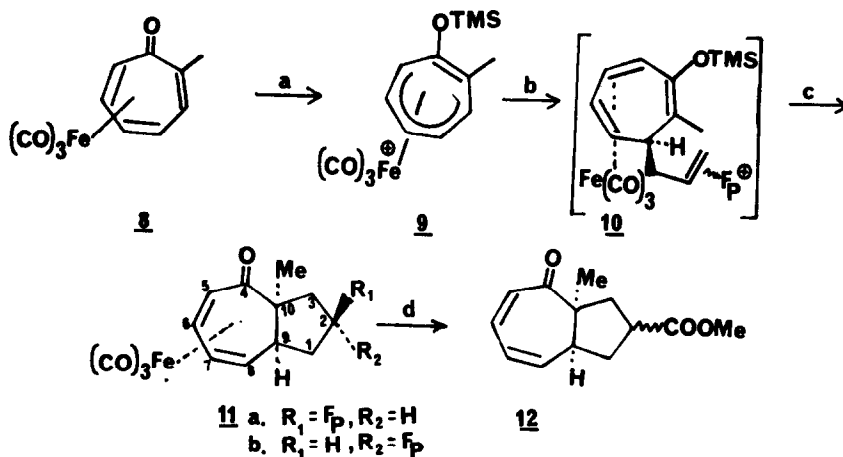
Summary: A short synthesis of the 10-methyl-4-keto-hydroazulenes, using organoiron reagents, is described.

We recently showed that the condensation of tropyliumiron tricarbonyl salts 1 with organoiron complexes 2, 3, and 4 provides an efficient, one step synthesis of highly functionalized hydroazulene complexes 5, 6, 7 of potential use as intermediates in the synthesis of guaianolide sesquiterpenes¹. The formation of a single regioisomeric product in these reactions is remarkable since, like the parent tropyliumiron tricarbonyl cation² and its monoalkyl derivatives³, 1 represents one member of a fluxional system of rapidly interconverting isomeric complexes⁴.



We now find that the closely related tropylium salt 9, derived from 2-methyltroponeiron tricarbonyl⁵, also enters into regioselective cycloadditions with Fp activated olefins to give products of potential use as intermediates in pseudoquainolide synthesis.

Thus, when 2-methyltroponeiron tricarbonyl is converted to the cation 9, by treatment with TMS triflate and, without isolation, this is allowed to react with 2a, cycloadduct 11 is obtained in 64% isolated yield as a 2.2:1 mixture of stereoisomers 11a and 11b^{6 7}.

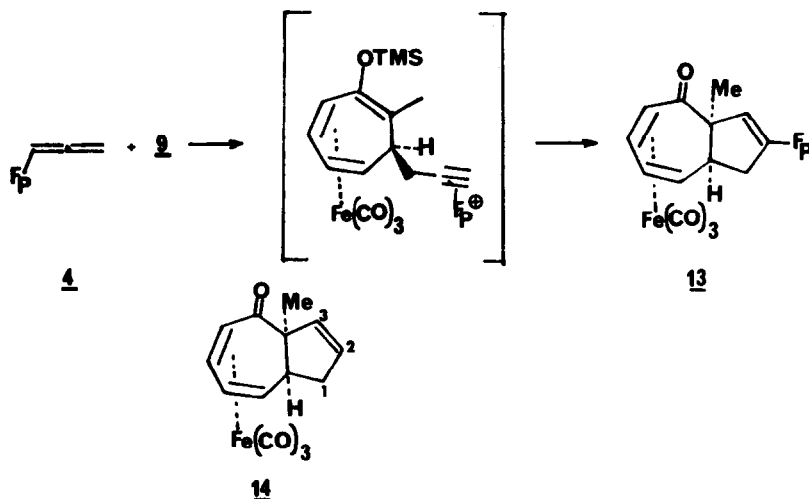


a. TMSTfI, CH_2Cl_2 , -78° b. 2a, CH_2Cl_2 , -78° 1 h c. 40° , 2 h d. $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, CO, MeOH, 0°

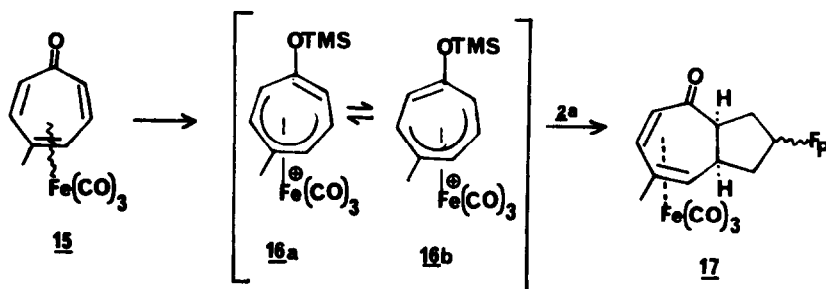
The structure of the cycloadduct was confirmed by treatment with ceric ammonium nitrate in methanol solution, which effects simultaneous replacement of the Fp group by carbomethoxy⁸ and removal of the $\text{Fe}(\text{CO})_3$ functionality⁹ to give 12. The structure of 12 is in turn supported by C-13 spin echo fourier transform experiments which show the presence of four vinylic CH carbons. In addition, the proton NMR spectrum of 12 shows two methyl singlet resonances at δ 1.20 and 1.22.

The formation of a single regioadduct requires that the operative tropyliumiron tricarbonyl tautomer in these reactions have structure 9, and that this cation reacts preferentially with (n' -allyl)Fp 2a at C-7 to give intermediate 10. Subsequent closure to the 5-membered ring by reaction of the enol silyl ether with the cationic olefin center then yields 11.

In a similar manner, reaction of complex 4 with tropylium ion complex 9 gave 13 in 61% yield as the only cycloadduct. Selective degradation of this compound by treatment at room temperature with 0.2 M HCl gave 14 in 81% yield. The position of the uncomplexed double bond in this product is supported by lanthanide shift reagent C-13 NMR studies using Eu-resolve¹⁰, which show paramagnetic shifts for C-2 and C-3 of 1.4 and 2.7 ppm respectively, but a shift of only 0.58 ppm for C-1.



Finally, when 4-methyltroponeiron tricarbonyl¹¹ 15 is converted to its tropyliumiron tricarbonyl complex and this is allowed to condense with 2a, a single cycloadduct is obtained in 41% yield. The C-13 NMR spectrum of this shows it to possess structure 17¹². The reaction path for this cyclization, as for the reactions of the tropylium ion complexes 1 and 9, is consistent with the effective reactive component being that one in which the silyloxy group is substituted on the uncomplexed double bond. In the present circumstance, two such tautomers 16a and 16b, are possible and the reaction appears to proceed through initial attack of 2a at the least encumbered terminus of the pentadienyl ligand of either of these isomers.



Further elaboration of these reactions is being examined.

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References

1. J. C. Watkins and M. Rosenblum Tet. Lett. 25, 2097 (1984).
2. J. E. Mahler, D. Jones, R. Pettit J. Am. Chem. Soc. 86, 3589 (1964).
3. C. P. Lewis, W. Kitching, A. Eisenstadt, M. Brookhart J. Am. Chem. Soc. 101, 4896 (1979).
4. Results of crossover experiments suggest that the first step in the two step cycloaddition reaction (see for example, 9→10→11) is irreversible under the reaction conditions.
5. Prepared by treatment of 2-methyltropone (W. T. Brady and J. Hieble Tet. Lett. 37, 3205 (1970)) with $\text{Fe}_2(\text{CO})_9$ in benzene at 50° for 90 min.
6. All new compounds reported gave satisfactory C,H analysis as well as ^1H and ^{13}C spectra compatible with the structures assigned.
7. Relative stereochemistries at the ring junction centers with respect to the iron tricarbonyl group in 11 as in 5, 6, and 7 is predicated on the well established trans addition of nucleophiles to tricarbonyl pentadienyliron cations. A. J. Pearson Acc. Chem. Res. 13, 463 (1980). The stereochemistry at C-8 is assigned on the basis of C-13 chemical shifts: 11a C-2,9,10: δ 16.54, 60.51, 54.03; 11b C-2,9,10 δ 19.72, 57.81, 55.37.
8. a) K. M. Nicholas, M. Rosenblum, J. Am. Chem. Soc. 95, 4449 (1973). b) R. S. Glass and W. W. McConnell Organometallics 3, 1630 (1984).
9. N. Genco, D. Marten, S. Rahgu, M. Rosenblum J. Am. Chem. Soc. 98, 848 (1976).
10. Eu-resolve (Alfa Chemicals), Eu(III) 2,2,6,6-tetramethylheptanedionate.
11. 4-Methyltropone was prepared from p-anisole following the procedure employed by A. J. Birch and R. Keeton, J. Chem. Soc. C 109 (1968) in the synthesis of 4-isopropyltropone.
12. Based on correlation of the C-13 chemical shifts of C-5,6,7 and 8 in the spectra of 5,6,7,11,13 and 17

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