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TETRACYCLO[4.4.0.0.^{2,5}0^{7,10}]DECANES: DIRECT SYNTHESIS FROM CYCLOBUTADIENEIRON TRICARBONYL AND DIENOPHILIC ACETYLENES

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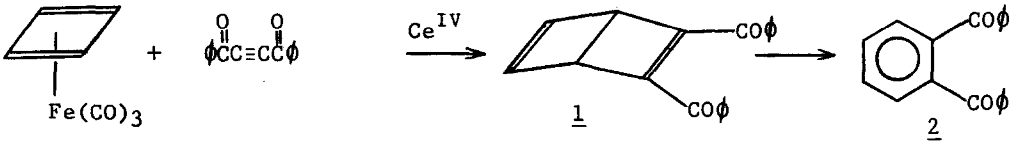
In a poineering publication, Pettit and co-workers reported that the ceric ion oxidation of cyclobutadieneiron tricarbonyl liberates cyclobutadiene, which can be trapped in the presence of acetylenes to yield derivatives of bicyclo[2.2.0]hexa-2,5-diene ("Dewar benzene").[1] We have found that certain bicyclo[2.2.0]hexadienes formed in this manner can undergo further reaction with a second equivalent of cyclobutadiene generated _in situ_, affording a convenient synthesis of some novel tetracyclic adducts.

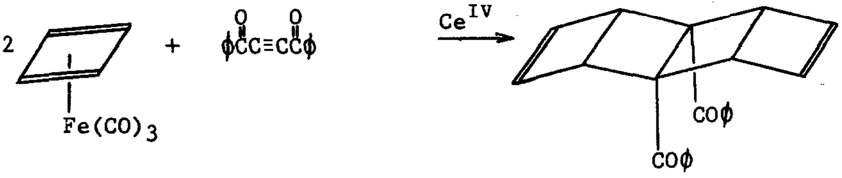
The addition of ceric ammonium nitrate to an ice-cold acetone solution of cyclobutadieneiron tricarbonyl[2] (one eq.) and dibenzoylacetylene[3] (one eq.) gave as the major product the expected 2,3-dibenzoylbicyclo[2.2.0]hexa-2,5-diene (1). This compound is isomerized completely to 1,2-dibenzoylbenzene (2) in about 24 hours at



room temperature. In comparison, the parent hydrocarbon, bicyclo[2.2.0]hexa-2,5-

diene, is reported to have a half-life of about two days at room temperature.[4]

When *two* equivalents of cyclobutadieneiron tricarbonyl were oxidized in the presence of one equivalent of dibenzoylacetylene, the major product was no longer 1, but rather a 2:1 adduct identified as 1,6-dibenzoyltetracyclo[4.4.0.0.^{2,5}0^{7,10}]deca-3,8-diene (3) (mp 97-98°).[5,6] We believe this to be the first synthesis of a compound containing four linearly fused cyclobutane rings.



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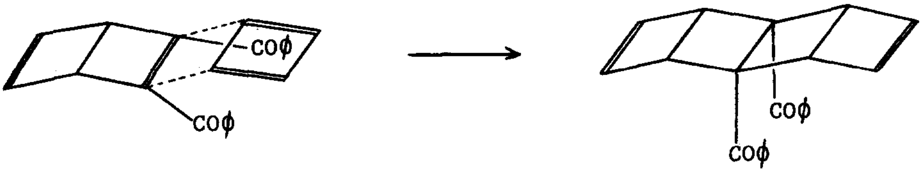
The Diels-Alder addition of cyclobutadiene to 1 would be expected to proceed *via* preferential approach of the diene to the less hindered (*exo*) face of the dienophile, with maximum overlap of unsaturated centers, giving rise to the stereochemistry shown in formula 3.



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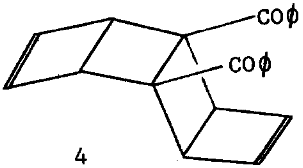
Other, less likely orientations of the reactants would yield the stereoisomeric tetracyclo[4.4.0.0.^{2,5}0^{7,10}]deca-3,8-dienes 4 or 5. The least symmetrical possibility, 4, is easily eliminated from consideration, since the nmr spectrum of the adduct shows only one type of olefinic proton (τ3.97, doublet, J = 1.5 Hz) and one type of bridgehead proton (τ6.28, doublet, J = 1.5 Hz). Reduction of 3 with sodium borohydride gave the corresponding diol, whose nmr spectrum shows the olefinic protons shifted downfield to τ3.46. This suggests that the olefinic protons of the



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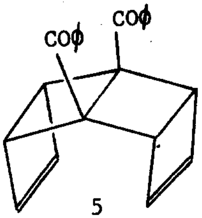

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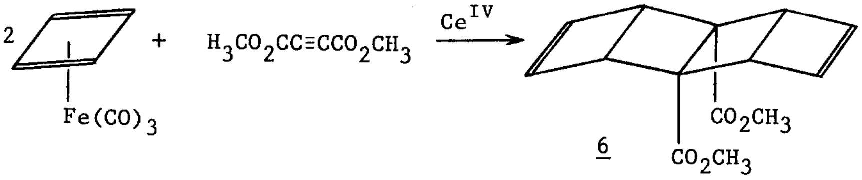
original diketone had been shielded by its ketonic substituents, a phenomenon that could occur with 3 but cannot be as easily reconciled with the stereochemistry of 5.

Another representative of this tetracyclic ring system was obtained by using dimethyl acetylenedicarboxylate as the dienophile. Once again, the symmetrical structure of the major product, 1,6-dicarbomethoxytetracyclo[4.4.0.0.^{2,5}0^{7,10}]deca-3,8-diene[6,7] (6) (mp 63-64°), was indicated by its simple nmr spectrum, which shows



only three absorptions (with the expected intensities) at τ3.63 (doublet, J = 1.5 Hz), 6.32 (singlet) and 6.65 (doublet, J = 1.5 Hz).

The addition of cyclobutadiene to acetylenes to produce bicyclo[2.2.0]hexa-2,5-dienes which can then react with a second equivalent of diene appears to represent a convenient, general route to the previously unknown tetracyclo[4.4.0.0.^{2,5}0^{7,10}]-deca-3,8-diene ring system. We hope to explore the chemistry of these compounds in the future.

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References and Footnotes

1. L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3253 (1965).
2. R. Pettit and J. Henery, *Organic Syntheses*, **50**, 21 (1970).
3. R. E. Lutz and W. R. Smithey, *J. Org. Chem.*, **16**, 51 (1950).
4. E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **85**, 3297 (1963).
5. The yield of **3** after isolation by preparative tlc was 17%, however, an attempt has not yet been made to optimize the reaction conditions or isolation procedure.
6. Infrared, nmr, and mass spectra, as well as elemental analytical data, were in accord with the assigned structure.
7. The yield of **6** after isolation by preparative tlc was 11%. No attempt has yet been made to optimize the procedure.