

SYNTHETIC APPLICATIONS OF SOME METAL CARBONYL COMPLEXES

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Abstract - The stoichiometric use of metal carbonyl complexes in organic synthesis offers many possibilities for the selective activation of unsaturated molecules or the stabilization of very reactive substrates.

Some results obtained in our group with iron and, to a lesser extent, manganese complexes are presented with emphasis on the following aspects :

- the chemical transformations which result from the process of complexation or decomplexation

- the modification of reactivity which accompanies complexation

- the protection of unstable species by ligation, which allows their further use in synthesis

- and the possibilities of asymmetric synthesis by transfer of the planar chirality of π -complexes to newly formed carbon centers.

This is exemplified further by some regio and stereocontrolled syntheses of natural products like tropolones, chrysanthemic acid derivatives and insect pheromones from different diene, trimethylenemethane and alkyne complexes.

INTRODUCTION

Synthetic applications of organometallic complexes belong to one of the frontier areas of present organic chemistry. Besides the huge amount of fruitful work done in catalytically promoted reactions, the stoichiometric use of transition metal π -complexes to accomplish strategic synthetic transformations is still a growing field.

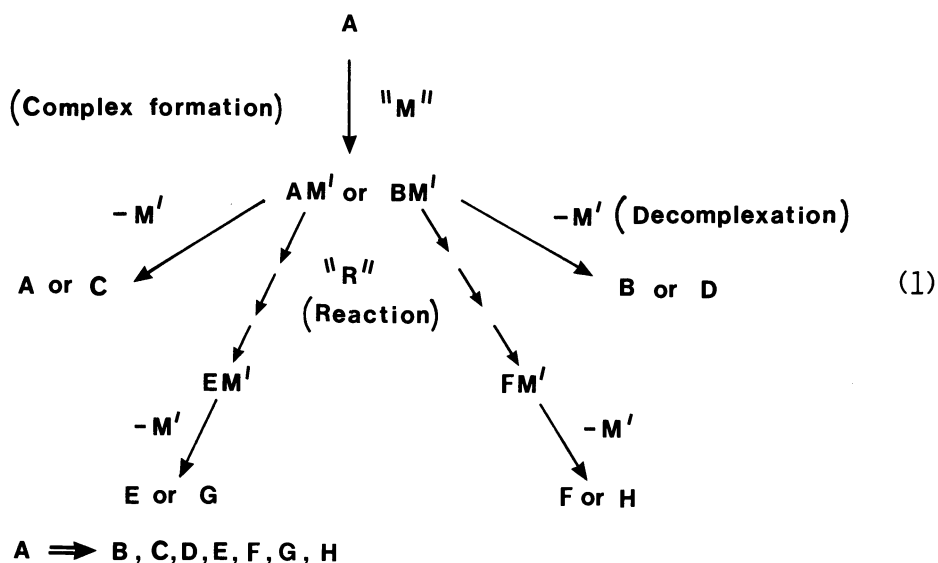
Our own interest was mainly focused to metal carbonyl complexes of iron and manganese.

These "ferrymen" metals form easy accessible, lowcost and relatively stable complexes from which the transformed organic ligands can in turn generally be recovered without problem. The last point is actually an important prerequisite when the synthesis of purely organic compounds is intended.

The complexation of an organic molecule formulated as A can be at the origin of several transformations, schematically depicted in the following manner (Scheme 1).

In this scheme "M" represents the symbol for the metallic complex-forming reagent, where "R" symbolises one or several other reagents, each letter designing another organic structure. Structural changes can be brought about at the stages of complexation or decomplexation or via chemical reactions on the complexes themselves. Obviously these transformations are only of interest for synthetic purposes if they cannot be achieved more simply on the uncomplexed ligands.

We will now describe several synthetic applications of complexation belonging to one or the other of these types.



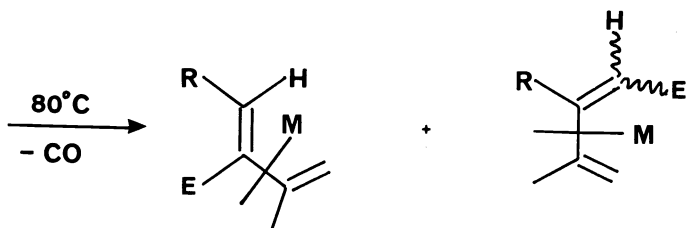
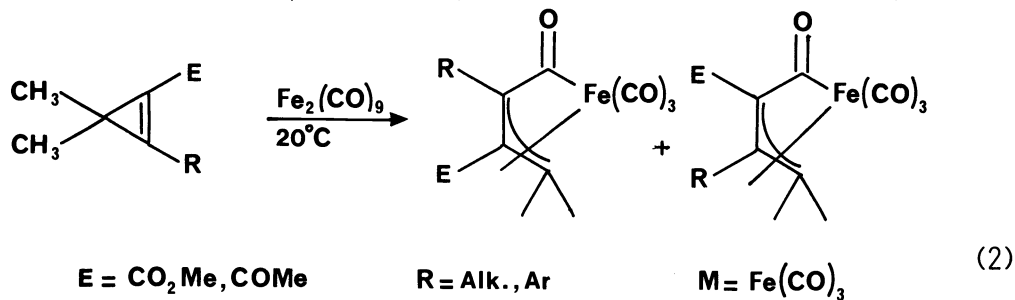
RESULTS and DISCUSSION :

1°) Structural modifications by complexation - decomplexation :



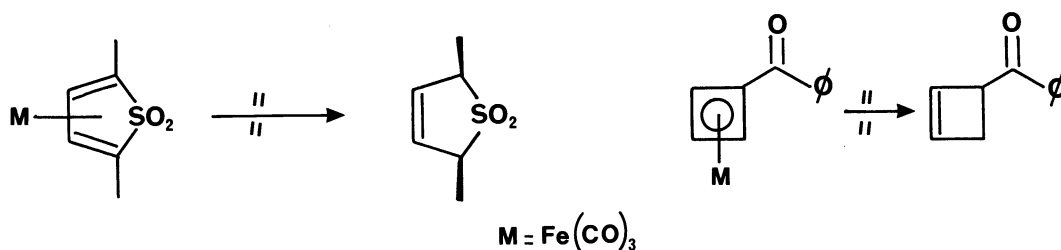
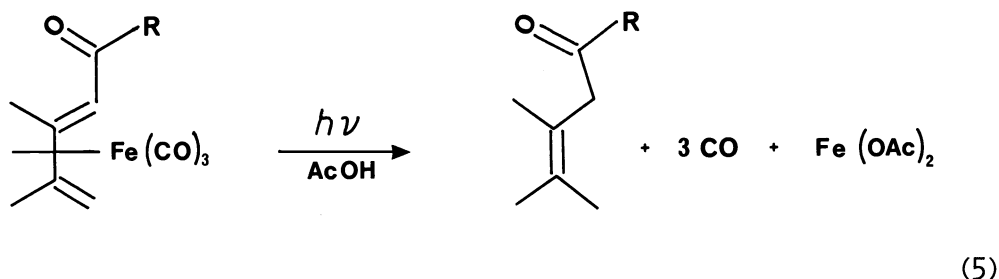
a) Complexes from electrophilic cyclopropenes : A → D

Certain methyl- and phenyl-substituted cyclopropenes were shown to react with iron carbonyls via ring opening and carbonylation to yield ($\eta^3 : \eta^1$ allylcarbonyl) iron tricarbonyl complexes (1). In our investigations, starting from the easily accessible electrophilic gem-dimethylcyclopropenes (2), these complexes were obtained in excellent yields. They show however as a new property the tendency to be easily transformed into isoprenic diene-iron tricarbonyl complexes (3), this result being achieved either thermally with loss of carbon monoxide or photochemically without carbon monoxide evolution (Scheme 2).



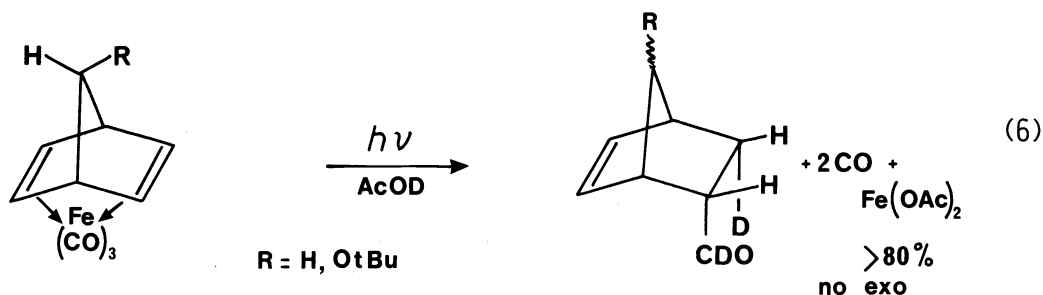
c) Photoreductive decomplexation : $A \rightarrow C$

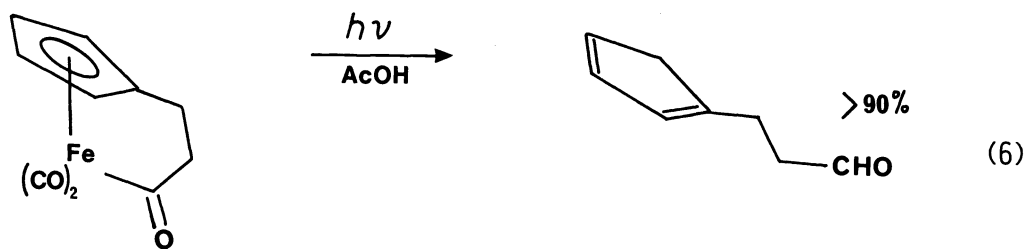
The commonly employed decomplexation methods for metal-carbonyl complexes make generally use of oxidative reagents. Besides Fe(III) and Ce(IV) salts, trimethylamine oxide is now widely used (6) although the cheaper reagent $H_2O_2/NaOH$ seems to be as effective (7). With these reagents, the organic ligands are generally recovered unchanged. This is not the case with the photodecomplexation method we discovered (8), which shows several interesting features. For example functionalized iron-tricarbonyl diene complexes, when irradiated in acetic acid, lead nearly quantitatively to hydrogenated compounds in a regio- and stereospecific process, the ligands being reduced to β,γ -functionalized monoolefins (Scheme 5).



The easy acylation of diene complexes under Friedel-Crafts conditions (9) makes this photodecomplexation method particularly interesting, especially when complexes of non-isolable ligands are involved. More conventional methods would lead in this last case to greatly modified structures whereas reductive photodecomplexation permits the use of the cyclobutadiene iron-tricarbonyl complex for a novel cyclobutene synthesis.

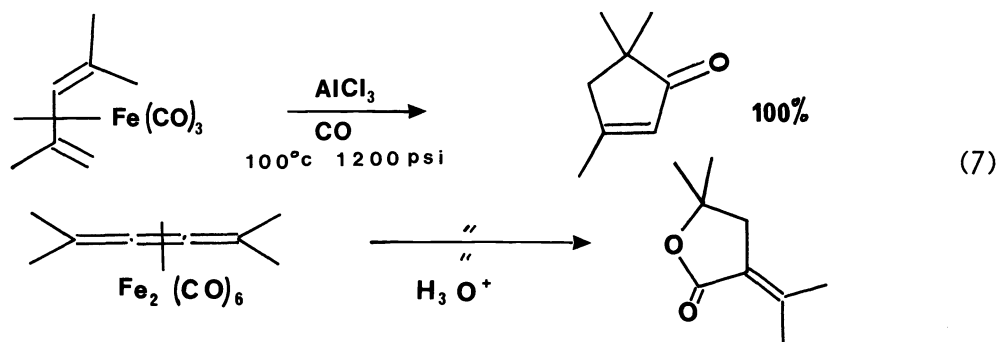
Unfunctionalized iron-tricarbonyl complexes of simple dienes do not lead to such clean-cut results by photolysis in acidic medium (10). We found however that complexes of unfunctionalized strained homodienes like norbornadienes undergo a rapid photoreductive decomplexation together with a stereospecific carbonylation. The first photochemical step may, in this case, be the intermediate formation of a coordinatively unsaturated acyl complex, in good agreement with the behaviour of a similar isolated acyl complex (Scheme 6).





d) Decomplexation with carbonylation : $A \longrightarrow C$

The aluminum trichloride promoted transformation of an o.xylylene iron-tricarbonyl complex into an indanone in ca. 50 % yield (11) seems not to be a preparatively valuable general reaction. However during a study on the scope and limitations of such a decomplexation method, performed under CO pressure on acyclic diene complexes (12), we found that suitably polysubstituted derivatives undergo the reaction very well. In addition we found that certain dinuclear iron complexes can be decomplexed similarly as shown by the example of the permethylated butatriene diiron hexacarbonyl complex (Scheme 7).



All these reactions show that simply by complex formation followed subsequently by decomplexation, several valuable structural changes can be achieved on suitable molecules. Chemical reactions on such formed complexes open however, much broader possibilities owing to the reactivity modification of the organic ligands as compared with the free molecules.

2°) Modification of the reactivity of the ligand

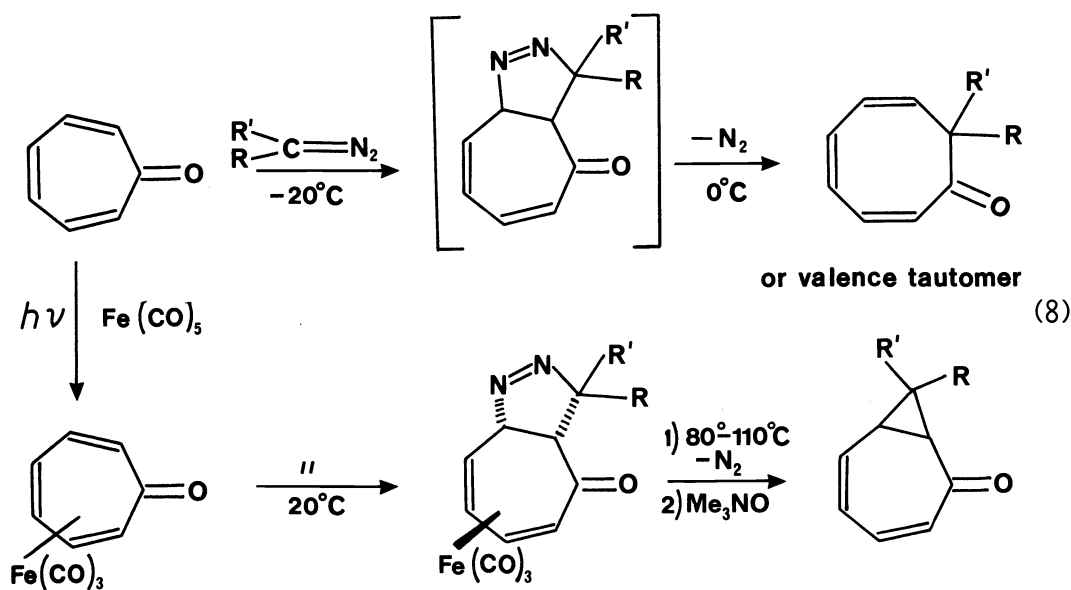


The following examples belong to the category of cycloaddition reactions of partially coordinated polyolefins.

Troponone is now a readily available (13) yet fascinating molecule, whose coordination with iron-tricarbonyl results in more or less predictable reactivity changes we may make use of. On the other hand the total synthesis of chrysanthemic acid derivatives offers still some challenges to the organic chemist, especially in the field of asymmetric synthesis. Here too the use of iron complexes led us to a new stereospecific and highly enantioselective route to such compounds.

a) Homotropones :

cyclic α,β -unsaturated ketones or lactones react with dimethyldiazomethane (2-diazopropane, DAP) by 1,3-dipolar cycloaddition. The Δ^1 -pyrazolines obtained are however very labile and lead to β -isopropyl derivatives with spontaneous nitrogen evolution (14). The same direct β -isopropylation of tropone would lead to a straightforward synthesis of natural tropolones like β -thujaplicin. In fact, tropones react with diazoalkanes by 1,3-dipolar cycloaddition unfortunately in the unexpected sense, leading to cyclooctatrienones or their bicyclic valence tautomers by spontaneous decomposition of the intermediate reversed Δ^1 -pyrazolines (15). Partial coordination of tropone with iron tricarbonyl enhances the ketonic character of the molecule (16). In consequence one could imagine a reverseal of polarity for the uncomplexed enone part of the molecule which should finally lead to the desired isopropylation. The effect of complexation with iron tricarbonyl is however not sufficient to reverse the direction of addition of diazoalkanes and the same type of Δ^1 -pyrazolines is obtained, but now as much more stable iron complexes. Their thermal decomposition, which requires temperatures up to 80°C to 110°C leads quantitatively to cyclopropanated tropone complexes. On decomplexation, good yields of the corresponding homotropones are given (Scheme 8).

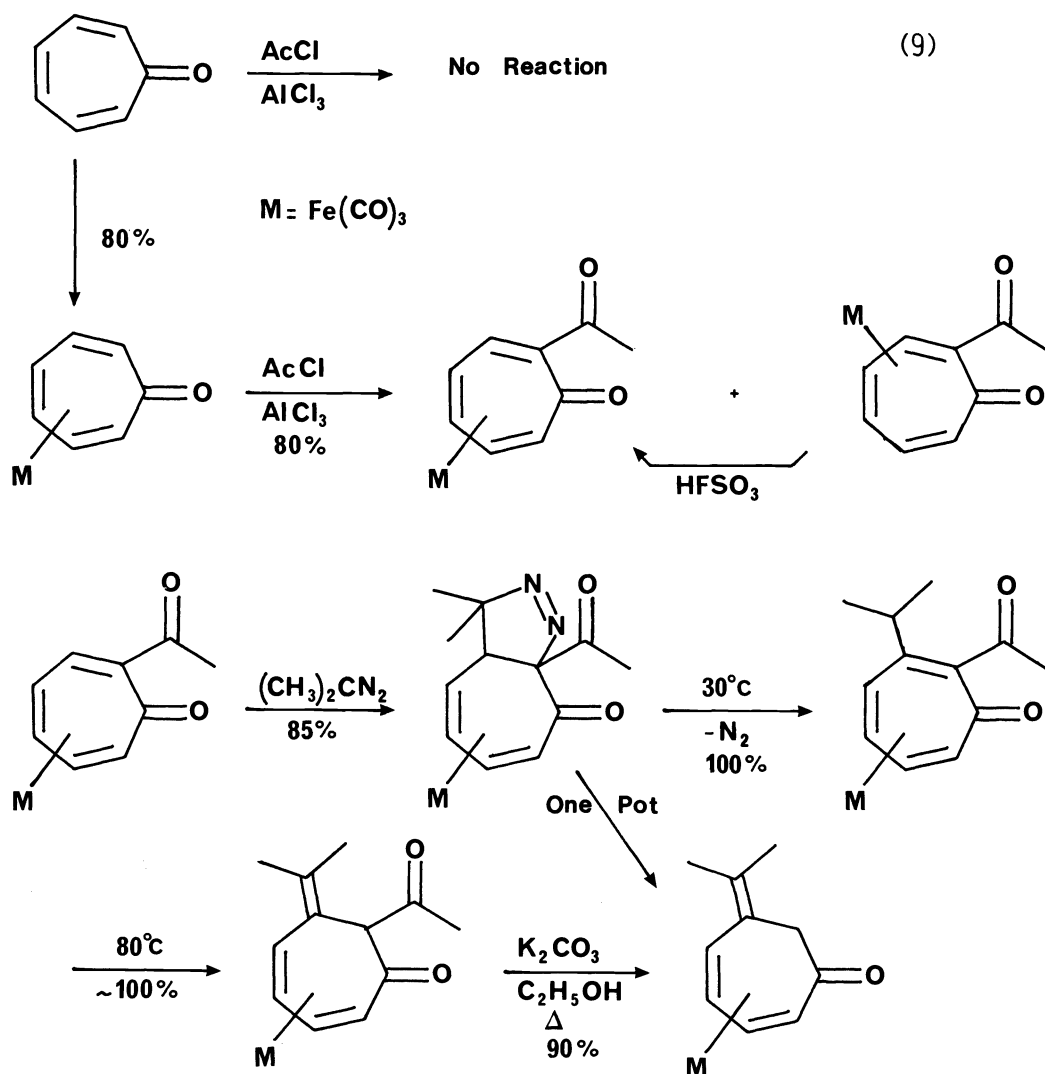


Diazoalkane	Pyrazoline	Thermolysis	Homotropones
R = R' = H	80 %	100 %	70 % overall
R = R' = CH ₃	90 %	100 %	80 % overall
R = CH ₃ R' = H	75 % (2 isomers)	84 % + 16 %	56 % + 11 % overall

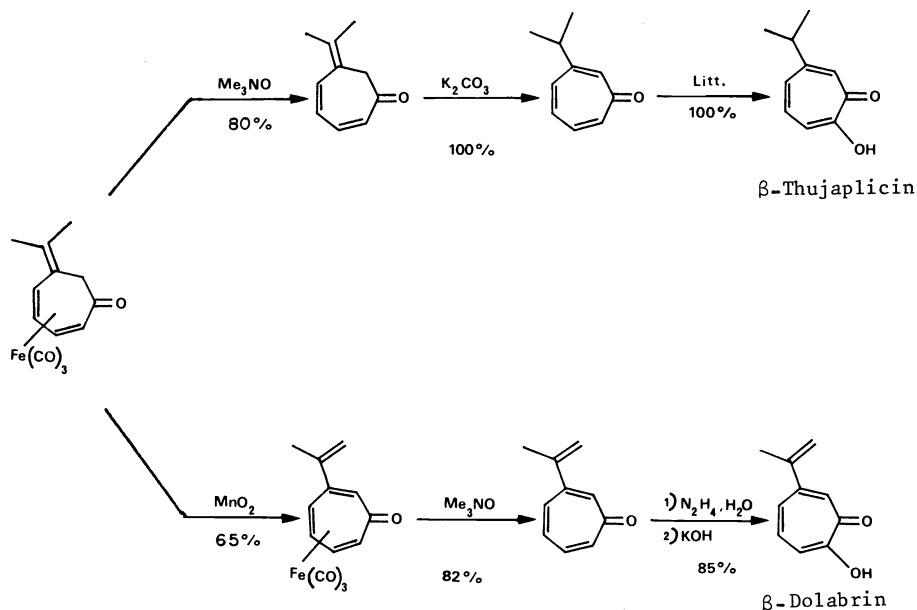
The specificity of the thermal decomposition and the fact that isomeric homotropone complexes are easily separated by chromatographic methods make this an efficient and versatile homotropone synthesis (17).

b) Natural tropolones :

The natural tropolones β -thujaplicin and β -dolabrin have rather simple structures (Scheme 10). In spite of this, only lengthy multistep or inefficient syntheses which do not start from tropone itself were published. The reason seems to lie in the fact that "no method has been known for the direct introduction of an alkyl group at C-3 position of troponoïd skeleton" (18). Since the direct isopropylation of tropone, or its iron tricarbonyl complex could not be achieved with dimethyldiazomethane we tried to take advantage of the presumed reactivity modification by complexation, to introduce, via Friedel-Crafts acylation, a directing substituent and thus achieve the required cycloaddition. Tropone and tropolones are indeed known to be reluctant to the Friedel-Crafts substitution reaction. On the contrary tropone-irontricarbonyl reacts with acetyl chloride in presence of aluminum chloride to give mixtures of two isomeric acetyltropone complexes with an overall yield of 80%. From the mixture of the slowly interconverting complexes, the desired one can be obtained nearly quantitatively by dissolution in HFSO_3 followed by quenching with aqueous base. The 1,3-dipolar cycloaddition leads now, as expected, to a different Δ^1 -pyrazoline and to the β -substituted derivatives (Scheme 9).



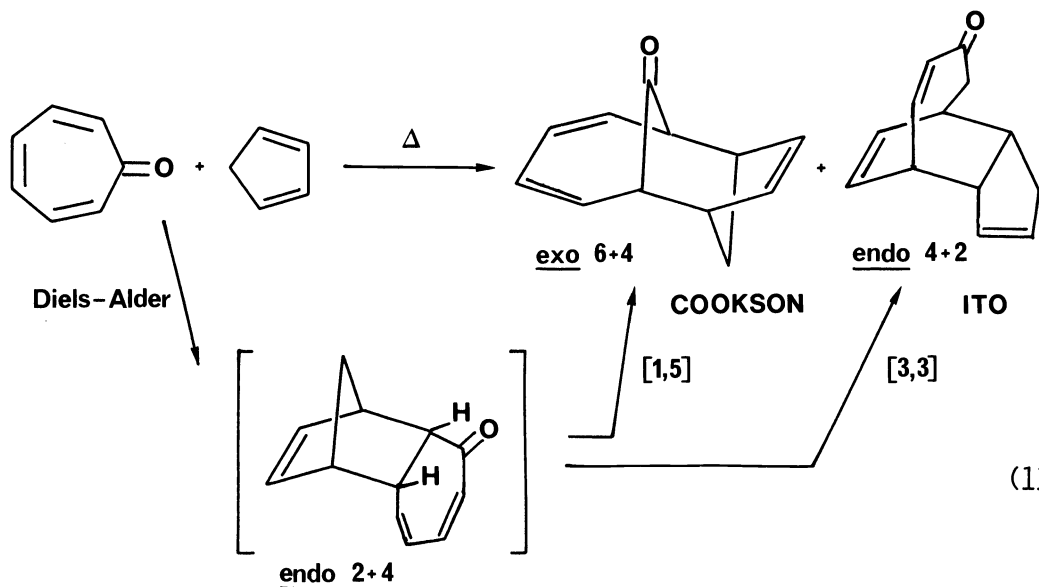
After alkaline β -diketone splitting, the β -thujaplicin synthesis is rapidly achieved by decomplexation followed by base catalyzed conjugation. The last step, i.e. the introduction of the phenolic hydroxyl, is a classical reaction of tropolone chemistry (Scheme 10). The more unsaturated tropolone β -dolabrin is readily available from the same isopropylidencycloheptadienone complex by dehydrogenation to β -isopropenyltropone-irontricarbonyl followed by similar final steps (19).



(10)

c) Diels-Alder cycloadduct of tropone :

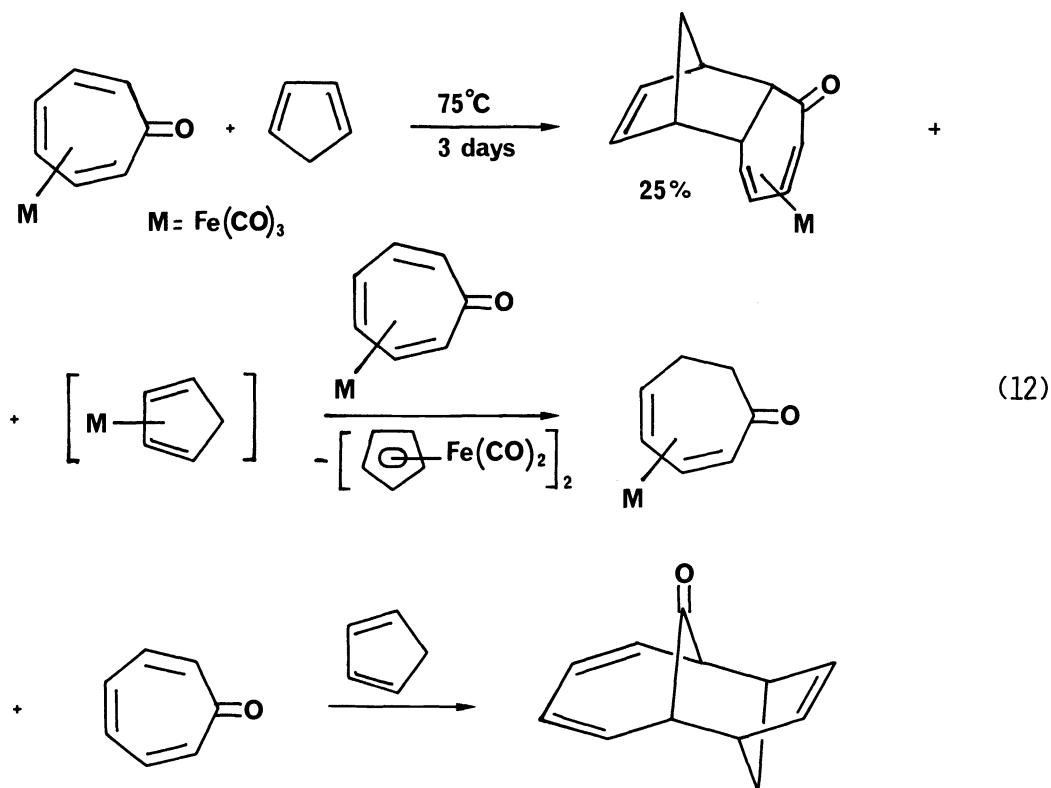
Tropone is known to react stereospecifically with cyclopentadiene at 80°C to exo-tricyclo (4.4.1.1.^{2,5}) dodeca-3,7,9-trien-11-one and at 145°C to endo-tricyclo (5.3.2.0.^{2,6}) dodeca-3,9,11-trien-8-one. (Scheme 11).



(11)

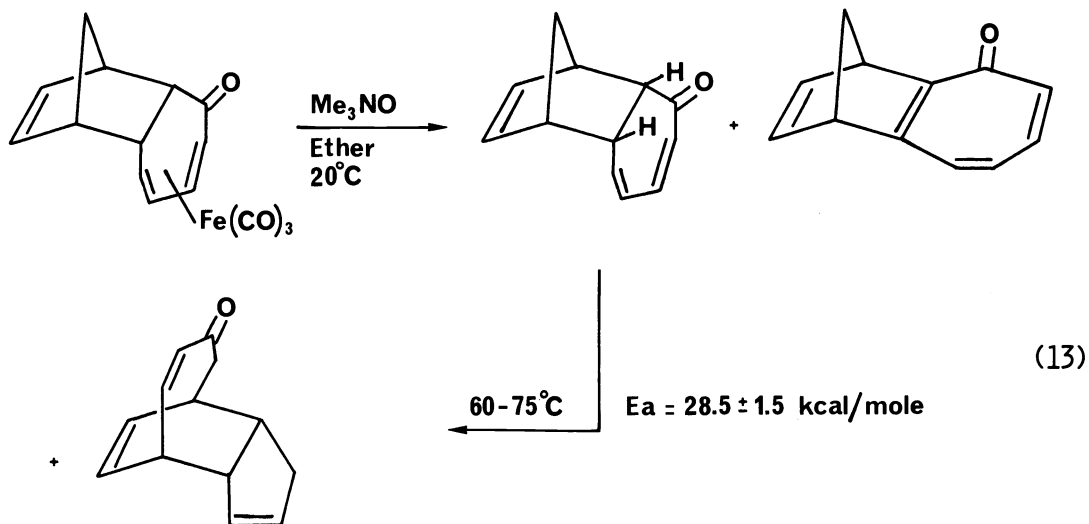
The formation of these adducts was respectively ascribed to concerted (6 + 4) electron and (4 + 2) electron cycloaddition reactions which are both thermally allowed processes (20), the given observed configurations being in good agreement with this explanation. Another mechanism of formation which would also lead stereospecifically to the same adducts can, however, be considered : i.e. the simple Diels-Alder addition of cyclopentadiene to tropone, acting as a simple enone, followed by thermally allowed [1,5] and [3,3] sigmatropic shifts.

Such a possibility cannot be ruled out a priori, as may be the temptation (21), unless it was invalidated by an independent synthesis of the hypothetical Diels-Alder intermediate. We could actually realize this synthesis by the simple Diels-Alder cycloaddition of cyclopentadiene with tropone-iron tricarbonyl (22). The determining advantage of choosing this method, aside from its simplicity, lies in the fact that the potentially very reactive cycloadduct is obtained under the "frozen" form of a metal complex. The experimental conditions must however be carefully adjusted owing to ligand exchange side reactions (Scheme 12).



On decomplexation under mild conditions, the uncomplexed Diels-Alder adduct of tropone is obtained as well as the isomerisation and dehydrogenation products. It represents a thermally very labile yet isolable compound which undergoes a clean conversion to Ito's adduct for low to medium conversion ratios where no trace of Cookson's adduct is observed (Scheme 13).

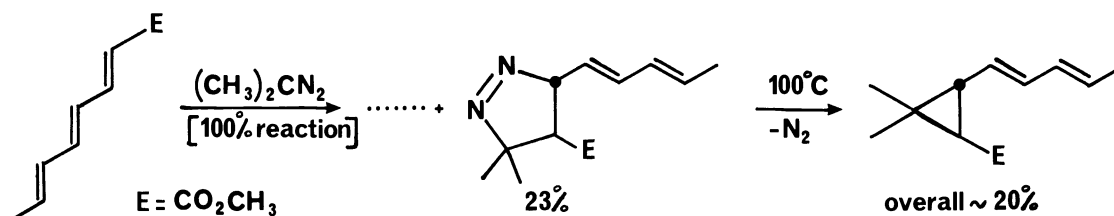
This shows that Cookson's adduct is actually the result of a direct cycloaddition, the same being not necessarily true for that obtained by Ito.



No 6+4 adduct detected

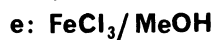
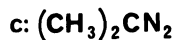
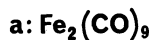
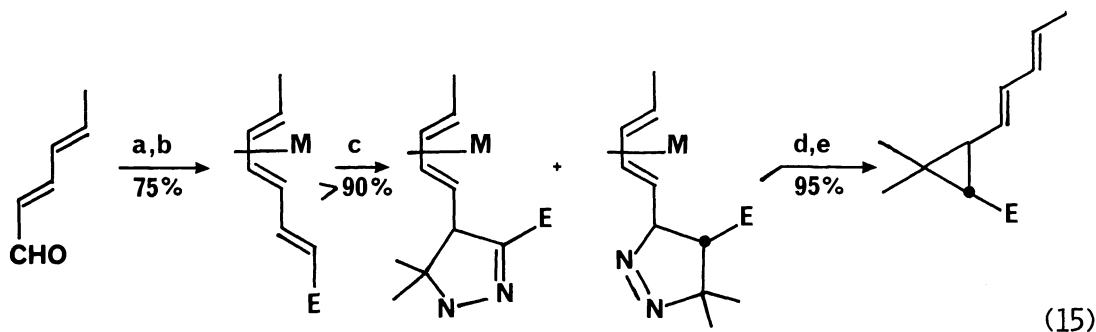
d) Chrysanthemic derivatives :

The reaction of dimethyldiazomethane with methyl octa-2,4,6 trieneoate yields a mixture of three pyrazolines which result solely from the cycloaddition to the more electrophilic α,β double bond. By thermolysis of the mixture, partial nitrogen elimination occurs with formation of different nitrogen-free products, among them being the desired dienic chrysanthemic analogue ($\sim 20\%$) formed via an isolable but minor Δ^1 -pyrazoline (23) (Scheme 14).

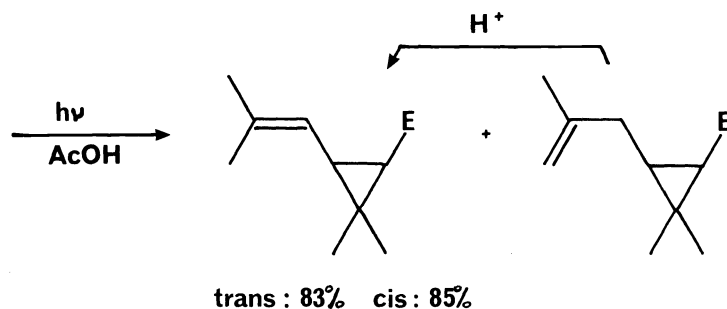
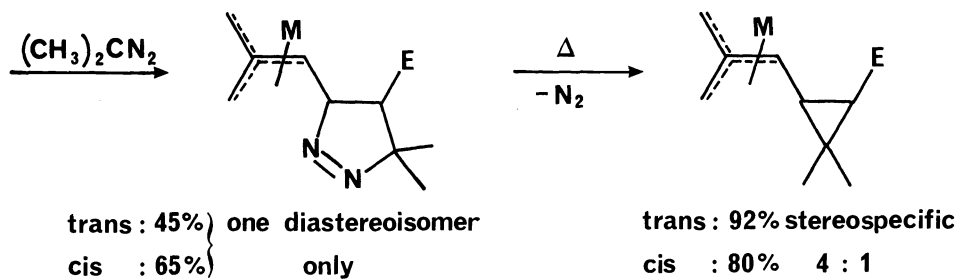
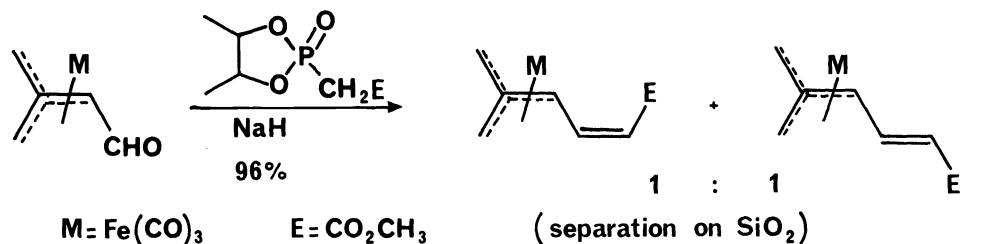


To improve on the yield we modified the course of the cycloaddition by complexation of the diene moiety. This was best achieved by Horner-Emmons reaction with the previously complexed sorbic aldehyde. The cycloaddition leads now to the complexed equivalent of the preceding Δ^1 -pyrazoline with only one other Δ^2 -pyrazoline as an easily separable minor component (24). Thermolysis followed by decomplexation yields the chrysanthemic analogue in more than 60% overall yield based on the complexed trienic ester (Scheme 15).

As shown, complexation affords only a partial but welcome reactivity modification in this case. The main advantage of the transient coordination lies here in the creation of a planar chirality which is of great utility for further asymmetric reactions as will be seen later in this report.



The same strategy starting from trimethylenemethane complexes led directly to the cis or trans chrysanthemates (Scheme 16). This was however only possible via our reductive photodecomplexation method, which permits the use of the trimethylenemethane complex as a chiral isoprenic synthon (25).



(16)

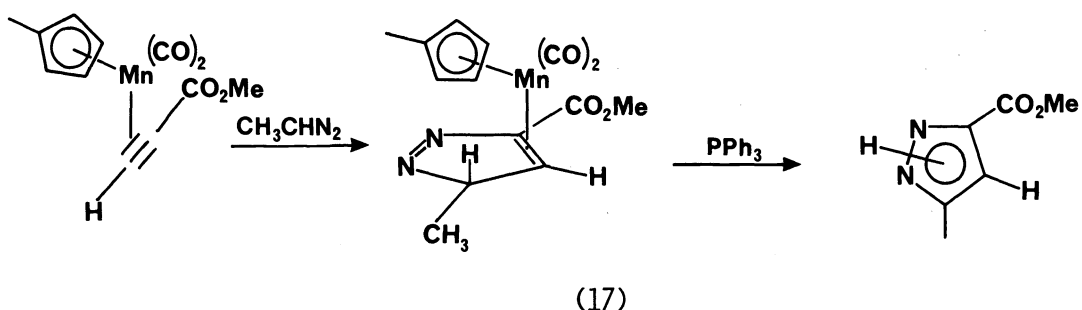
3°) Specific reactivity of some complexes ; Stabilization of unstable molecules by complexation :

Although the reaction described in this paragraph could have been considered in the previous section we have chosen to treat them separately, some ligands being unstable molecules and a direct comparison of reactivity is therefore difficult to achieve.

a) Electrophilic allenes :

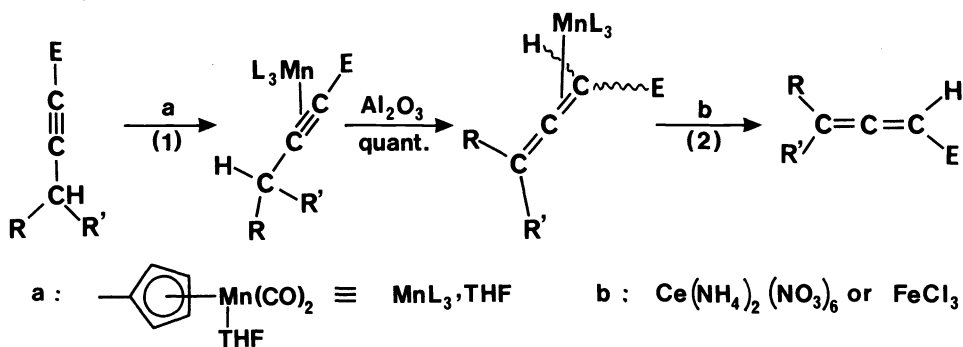
Dicobalthexacarbonyl alkyne complexes represent a well known protected form of acetylenic derivatives in organic synthesis (26).

Of much less importance in this connection are alkyne complexes in which the triple bond acts only as a two electrons ligand. We used such a partially protected alkyne manganese complex to synthesize stabilized tautomerizable 3H-pyrazoles (27) (Scheme 17).



Their evolution on photolysis is however rather disappointing being a simple isomerisation to nitrogen bonded 1H-pyrazole complexes. On using disubstituted acetylenic esters or ketones, bearing at least one hydrogen α to the triple bond, we could however observe an easy and quantitative isomerization to allene manganese complexes.

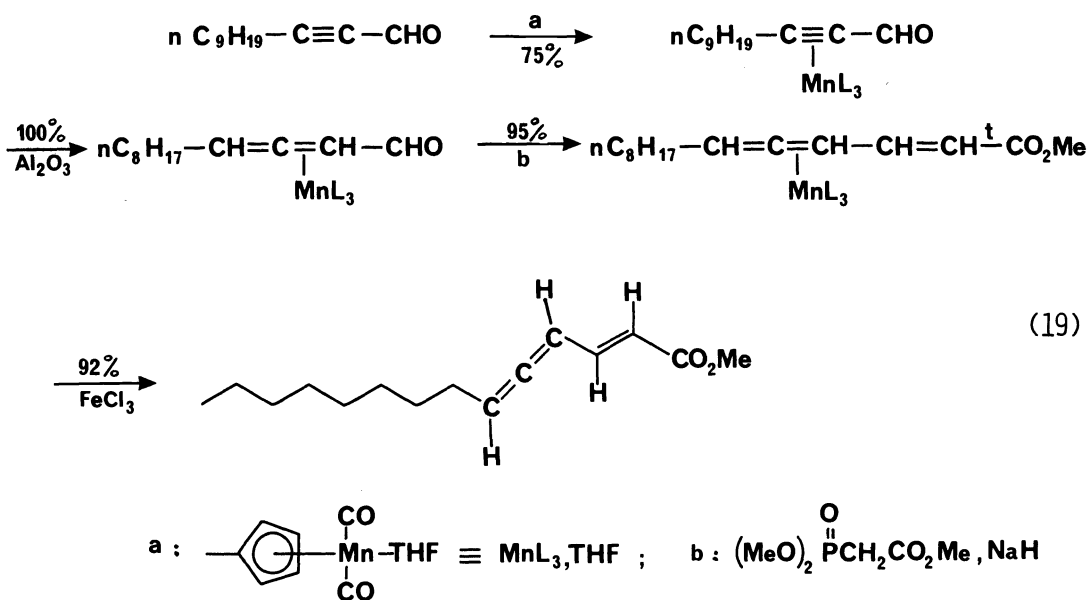
These represent air stable compounds which can be easily separated and purified without decomposition by liquid chromatography. The starting complex-forming reagent, methylcyclopentadienyltricarbonylmanganese, is a cheap material and isomerization proceeds readily in the presence of basic aluminum oxide. Since the oxidative cleavage of these complexes with iron (III) chloride, or better cerium (IV) ammonium nitrate usually proceeds with very good yields, this rearrangement constitutes a preparatively useful method for the synthesis of electrophilic allenes from readily accessible acetylenes (28) (Scheme 18).



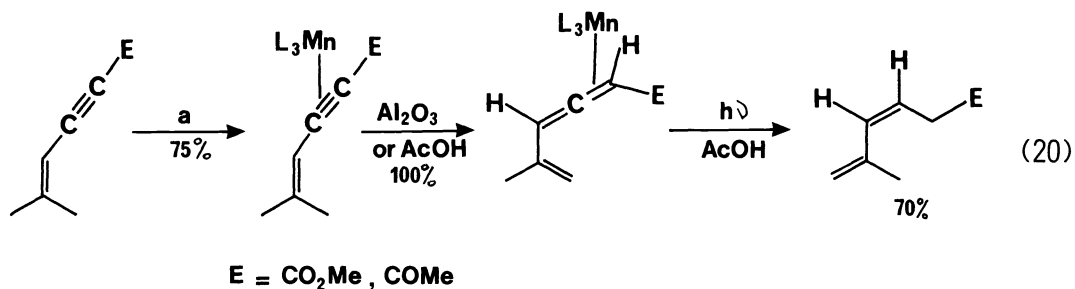
R	R'	E	(1)	(2)	b
H	H	CO ₂ Et	70 %	81 %	Fe III
C ₂ H ₅	H	CO ₂ Me	72 %	85 %	
nC ₄ H ₉	H	CO ₂ Me	75 %	95 %	
C ₂ H ₅	H	COCH ₃	70 %	70 %	Ce IV
(CH ₂) ₅		COCH ₃	70 %	72 %	
(CH ₂) ₅		CHO	70 %	71 %	
nC ₅ H ₁₁	H	CHO	75 %	unstable	

(18)

Special importance is attached to the allene complexes, in which the allene is present as a protected group. This is particularly obvious for allenic aldehydes which are generally unstable compounds, unless highly substituted. In the complexed form reactions can be carried out successfully whereas with free allenes only very poor yields are given due to this instability. The straightforward synthesis of the sexual pheromone of the male dried bean beetle is given as an illustration of this methodology (Scheme 19).



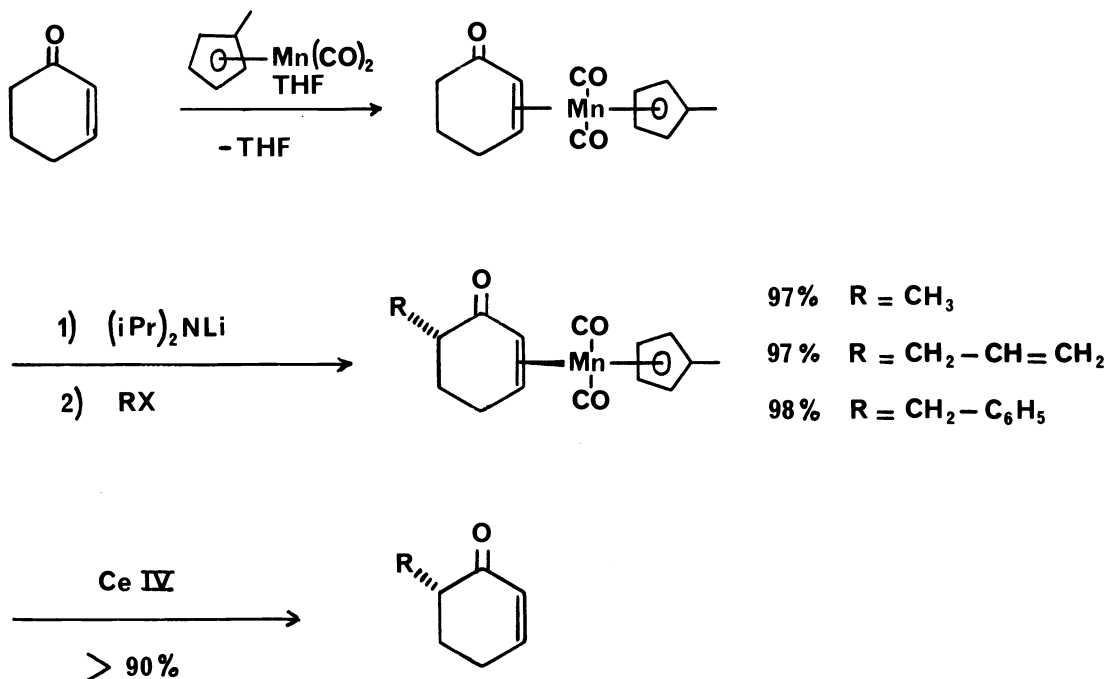
The preceding rearrangements are formally [1,3] hydrogen shifts. The formal [1,5] isomerization proceeds even more readily and stereospecifically, at least in the cases we have examined (Scheme 20).



The photocleavage in acetic acid, which is still effective with manganese dicarbonyl complexes, offers in this last case a new entry to E, Z substituted dienes (28).

b) α' -alkylation of α -enones :

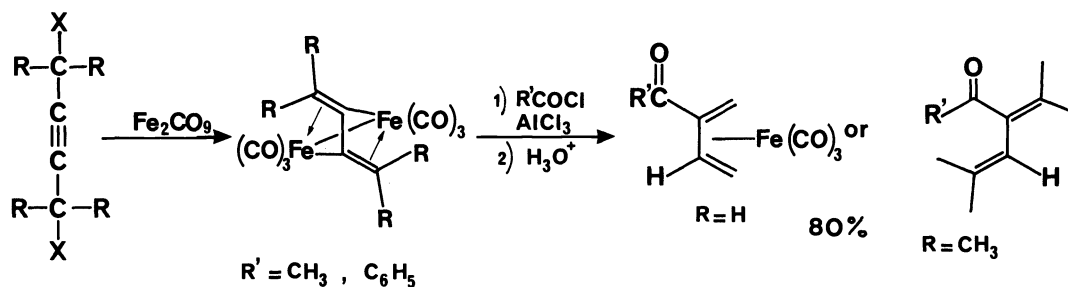
The cyclopentadienyl manganese dicarbonyl protecting group appears to be very stable against strong bases. We took advantage of this feature to achieve the regiospecific α' -alkylation of cyclic α -enones like cyclohexenone (29). Lithium diisopropylamide is a suitable base for this purpose. Markedly the electrophile attacks solely from the exo side, giving nearly quantitatively one single diastereoisomer (Scheme 21). This specificity holds promise toward asymmetric synthesis.



(21)

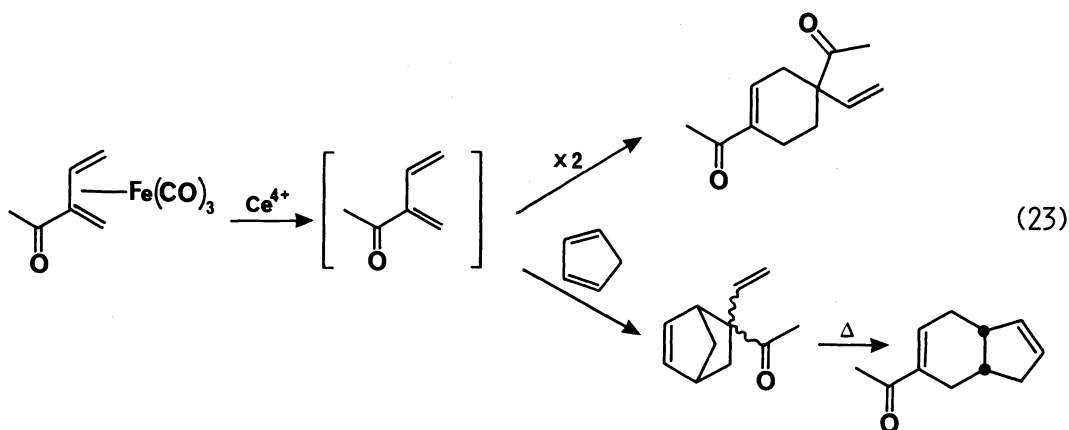
c) 2-Acylbutadienes :

Butadiene and simple methylated butadienes, as tricarbonyl-iron complexes, can readily be acylated in the 1-position under Friedel-Crafts conditions (9). In contrast, open chain 1,3-dienes which carry an acyl group in the 2-position are accessible only with difficulty. We found a route to 2-acylbutadienes using a reaction related to Friedel-Crafts acylation starting, however, from butadiene-diiron hexacarbonyl complexes (30). These are obtained directly by reaction of 1,4-dihalogenated 2-butyne with carbonyl-iron compounds (31). Acyl chlorides reacts with these dinuclear complexes in presence of aluminum chloride to give, after acidic work-up, 2-acylated butadienes, either as tricarbonyliron complexes or as free organic ligands, depending on the substitution pattern (Scheme 22).



(22)

The tetramethylbutatriene complex reacts to give the free, relatively stable, acyldiene. In contrast, we were unable to isolate the corresponding 2-acylbutadienes. The Diels-Alder dimer was obtained directly when the acetyl complex was cleaved, and in the presence of cyclopentadiene only Diels-Alder adducts with this diene were obtained (Scheme 23).



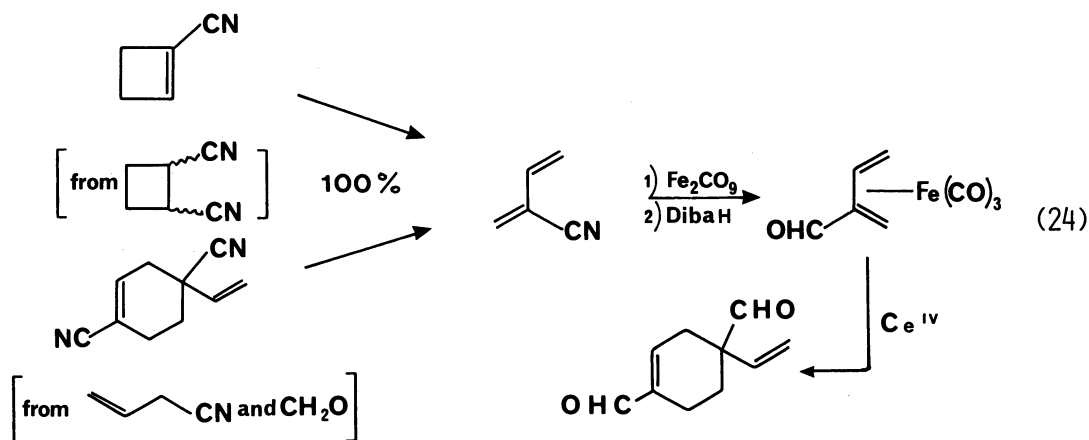
The very high reactivity and hence the non-isolability of 2-acylbutadienes makes it all the more important to obtain these dienes as stable tricarbonyliron complexes. This unusual increase in reactivity which contrasts strongly with that of similar 1-substituted butadienes has led us to study the corresponding aldehyde.

d) 2-Formylbutadiene: dithiane carbanions.

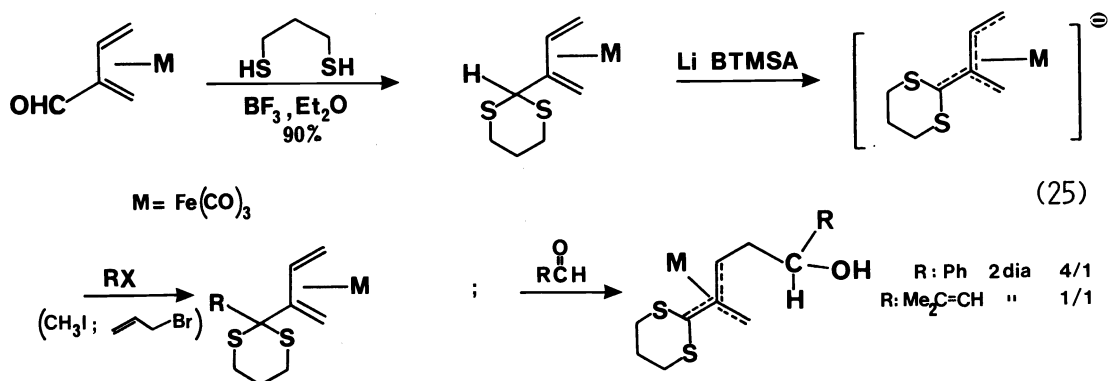
The stable iron tricarbonyl complex of this diene can be obtained from the corresponding methyl ester complex prepared as seen before from an allenic ester, or in several steps starting from isoprene (32).

A shorter approach is, however, via the isolable 2-cyanobutadiene by complexation and DibaH reduction (33). The diene nitrile is quantitatively obtained by valence isomerization of 1-cyanocyclobutene or retro-Diels-Alder reaction using flash-thermolysis conditions (Scheme 24). Both precursors are prepared in single step procedures from commercial products (34, 35).

As expected, the free aldehyde is unisolable and very reactive giving only the Diels-Alder dimer after cleavage of the complex. Different investigations were performed on this complex, among them dithiane formation and related carbanionic chemistry.



In contrast with the amount of work done with complexed cations, carbanions which are adjacent to iron tricarbonyl coordinated sites are only scarcely encountered (36). This led us to investigate dithiane carbanions derived from different aldehyde complexes. The iron tricarbonyl complex of 2-formylbutadiene reacts smoothly with propane-1,3-dithiol in presence of boron trifluoride etherate to the corresponding dithiane (90%). Lithium bis-trimethylsilylamide proved to be the most suitable base for carbanion formation in this case. A surprising result is the sharp dichotomy we observed in the reaction with alkyl halides on one hand and aldehydes or ketones on the other (37). With the former electrophiles, substituted dithiane diene complexes are obtained, while the second lead to sulfur substituted trimethylene-methane complexes (Scheme 25).



Such clean results were not observed with structurally different dithiane complexes. For instance the corresponding reactions starting from the complexed sorbic aldehyde or formyltrimethylenemethane led only to untractable mixtures of partially decomposed compounds. It seems therefore that the heterosubstituted trimethylenemethane substructure is essential for carbanion stabilization here.

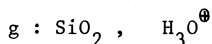
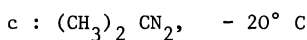
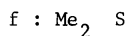
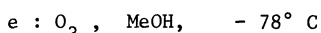
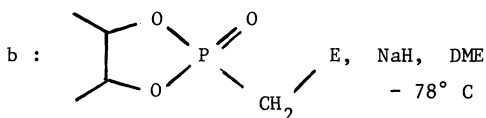
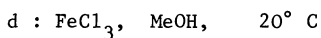
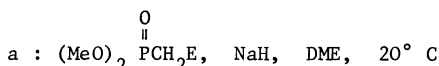
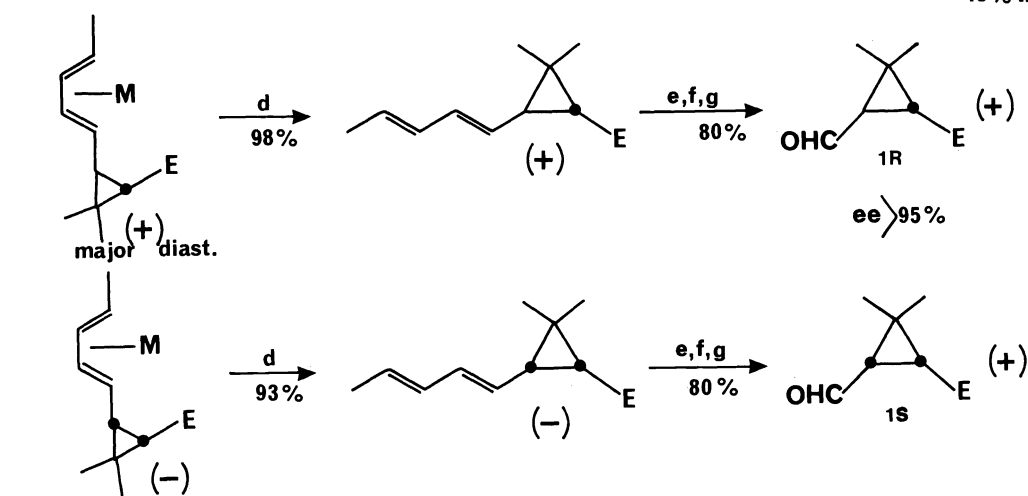
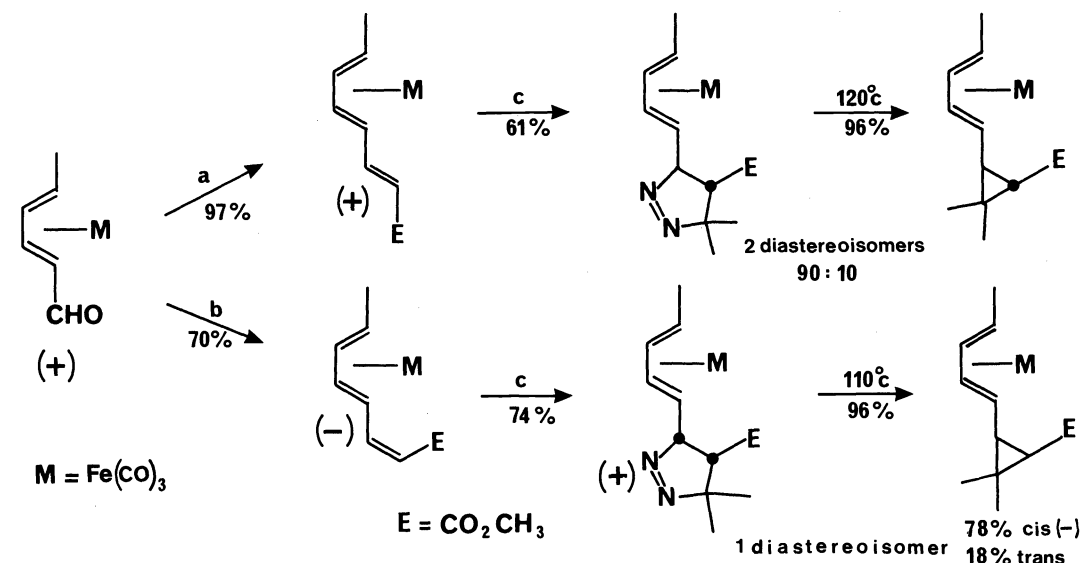
4°) Asymmetric synthesis : Hemicaronaldehydes

The planar chirality inherent to π -complexes of prochiral organic ligands can be transferred with more or less efficiency to carbon centers which are created by subsequent chemical reactions of these complexes. This principle could be applied with success to induce asymmetric synthesis of the cyclopropane ring of cis and trans hemicaronic aldehydes which are valuable key intermediates for the synthesis of pyrethroids (24, 38).

As detailed in section 2d, the use of the iron tricarbonyl complex of sorbic

aldehyde permits the synthesis of a dienic analogue of trans-chrysanthemate with an overall yield of 60%. The cycloaddition step, leading to Δ^1 -pyrazolines is in fact highly diastereoselective (2 diastereoisomers in the ratio 9 : 1) and the cyclopropanic diastereoisomers obtained by thermolysis are easy separable compounds. Since the starting aldehyde complex can be resolved easily and nearly quantitatively into its enantiomers via the diastereoisomeric semioxamazones, this opens a way to optically active derivatives which, by ozonolysis, give the trans hemicaronaldehydes in high enantiomeric excess (> 95%).

The use of a modified Horner reagent allows the use of the same reaction sequence in the cis series, with an even higher diastereotopic differentiation in the cycloaddition step (Scheme 26)



(26)

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REFERENCES

1. M.G. Newton, N.S. Pantaleo, R.B. King, C.K. Chu *Chem. Comm.* 10 (1979) ; P. Binger, B. Cetinkaya, C. Kruger *J. Organomet. Chem.* 159, 63 (1978) ; G. Dettlaf, U. Behrens, E. Weiss *Chem. Ber* 111, 3019 (1978)
2. M. Franck-Neumann, C. Dietrich-Buchecker, A. Khemiss *J. Organomet. Chem.* 220, 187 (1981)
3. M. Franck-Neumann, C. Dietrich-Buchecker, A. Khemiss *Tetrahedron Letters* 22, 2307 (1981)
4. M. Franck-Neumann, C. Dietrich-Buchecker, A. Khemiss *J. Organomet. Chem.* 224, 133 (1982)
5. F. Brion, D. Martina *Tetrahedron Letters* 23, 861 (1982)
6. Y. Shvo, E. Hazum *Chem. Comm.* 336 (1974)
7. M. Franck-Neumann, M.P. Heitz, D. Martina *Tetrahedron Letters* 24, 1615 (1983) ; cf W. Hieber, *Z. anorg. u. allg. Chem.* 204, 165 (1932) ; S.G. Davies *J. Organomet. Chem.* 179, C5 (1979)
8. M. Franck-Neumann, D. Martina, F. Brion *Angew. Chem.* 90, 736 (1978) - *Angew. Chem. Int. Ed. Engl.* 17, 690 (1978)
9. E.O. Greaves, G.R. Knox, P.L. Pauson *Chem. Comm.* 1124 (1969) ; R.E. Graf, C.P. Lillya *J. Organomet. Chem.* 166, 53 (1979) ; R. Pettit *Pure and Appl. Chem.* 17, 253 (1968)
10. F.W. Grevels *Habilitationschrift 1982 Schriftenreihe des Max-Planck-Instituts für Strahlenchemie n° 5, Mülheim a. d. Ruhr.*
11. B.F.G. Johnson, J. Lewis, D.J. Thompson *Tetrahedron Letters* 1974, 3789
12. M. Franck-Neumann and E.L. Michelotti, unpublished results
13. P. Radlick *J. Org. Chem.* 29, 960 (1964)
14. M. Franck-Neumann *Angew. Chem.* 80, 42 (1968) - *Angew. Chem. Int. Ed. Engl.* 7, 65 (1968)
15. M. Franck-Neumann *Tetrahedron Letters* 2143 (1970) ; M. Franck-Neumann, D. Martina *Tetrahedron Letters* 1755 (1975)
16. E. Weiss, W. Hübel *Chem. Ber.* 95, 1179 (1962)
17. M. Franck-Neumann, D. Martina *Tetrahedron Letters* 1759 (1975)
18. R. Noyori, S. Makino, T. Okita, Y. Hayakawa *J. Org. Chem.* 40, 806 (1975)
19. M. Franck-Neumann, F. Brion, D. Martina *Tetrahedron Letters* 5033 (1978)
20. R.B. Woodward, R. Hoffmann *Angew. Chem.* 81, 797 (1969)
21. K.N. Houk, R.B. Woodward *J. Amer. Chem. Soc.* 92, 4145 (1970)
22. M. Franck-Neumann, D. Martina *Tetrahedron Letters* 2293 (1977)
23. M. Miesch *Thèse de Doctorat-ès-Sciences Université Louis Pasteur Strasbourg 1981*
24. M. Franck-Neumann, D. Martina, M.P. Heitz *Tetrahedron Letters* 23, 3493 (1982)
25. The synthesis of optically active compounds is in progress since we could resolve the formyltrimethylenemethane complex. M. Franck-Neumann, M.P. Heitz, D. Martina, in preparation.
26. K.M. Nicholas, M.O. Nestle, D. Seyferth in "Transition metal organometallics in organic synthesis" Vol II H. Alper, Ed., Academic Press, New York, 1978, p. 1-63.
27. F. Brion *Thèse de Doctorat-ès-Sciences Université Louis Pasteur Strasbourg 1980*
28. M. Franck-Neumann, F. Brion *Angew. Chem.* 91, 736 (1979) - *Angew. Chem. Int. Ed. Engl.* 18, 688 (1979)
29. M. Franck-Neumann and M. Sedrati, unpublished results
30. M. Franck-Neumann, D. Martina, F. Brion *Angew. Chem.* 93, 900 (1981) - *Angew. Chem. Int. Ed. Engl.* 20, 864 (1981)
31. K.K. Joshi *J. Chem. Soc. (A)* 594 (1966)
32. M. Franck-Neumann, D. Martina, M.P. Heitz, unpublished results
33. M. Franck-Neumann, M. Sedrati and M. Mokhi, unpublished results
34. D.M. Gale, S.C. Cherkofsky *J. Org. Chem.* 38, 475 (1973)
35. C.C. Price, G.A. Cypher, I.V. Krishnamurti *J. Amer. Chem. Soc.* 74, 2987 (1952)
36. H. Maltz, B.A. Kelly *Chem. Comm.* 1390 (1971) ; M. Oda, N. Morita, T. Asao *Chem. Lett* 397 (1981) ; L.K.K. LiShingMan, J.G.A. Reuvers, J. Takats, G. Deganello *Organometallics* 2, 28 (1983)
37. M. Franck-Neumann, M.P. Heitz and D. Martina, in preparation
38. For a similar synthesis of chiral electrophilic cyclopropanes cf A. Monpert, J. Martelli, R. Grée, R. Carrié *Tetrahedron Letters* 22, 1961 (1981).