

STEREOSELECTIVE NUCLEOPHILIC ATTACKS ON CARBENIUM IONS GENERATED
FROM (1-INDANOL)- AND (1-TETRALOL)Cr(CO)₃ AS SYNTHETIC INTERMEDIATES.

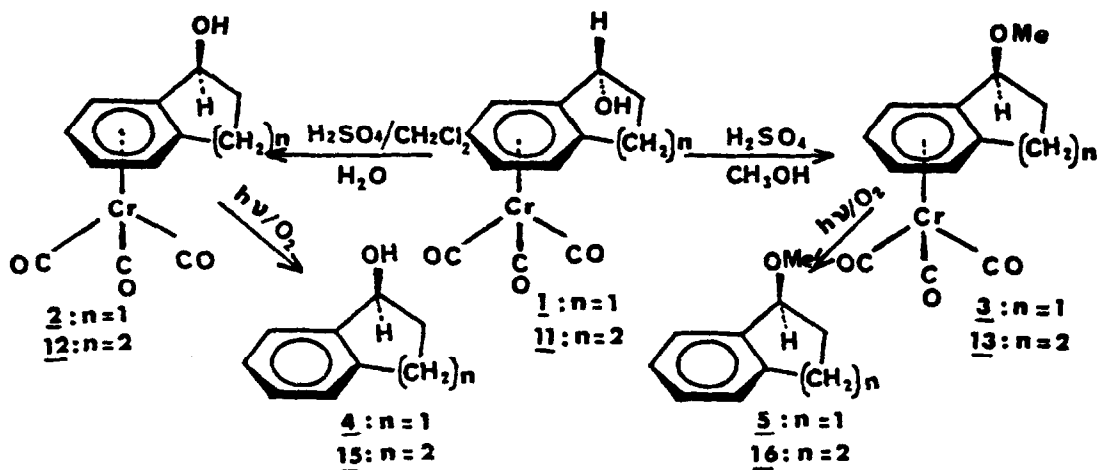
*Siden TOP, André MEYER and Gérard JAOUEN**

"Stéréochimie des Eléments de Transition",
Laboratoire de Chimie des Organométalliques, E.R.A. C.N.R.S. n° 477,
Université de Rennes, 35042 Rennes Cedex, France.

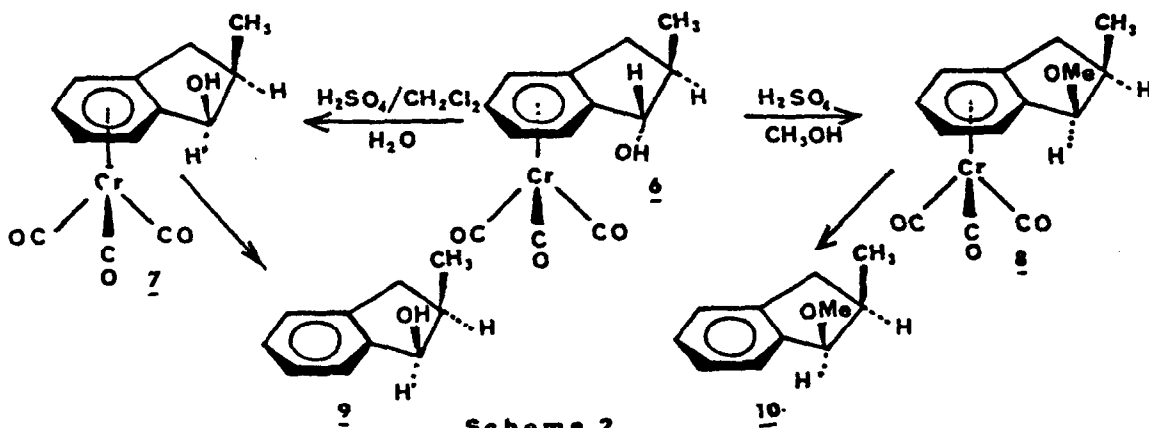
SUMMARY - *Temporary complexation of an arene ring by the Cr(CO)₃ unit bringing about both a considerably enhanced stabilization of adjacent carbenium ions and a total control of nucleophilic attack in an "exo" fashion allows important applications in organic synthesis.*

The remarkable stabilisation of carbenium ions contiguous to organic entities complexed by a transition metal is a well-known characteristic in organometallic chemistry. A great deal of controversial study has been devoted to the intrinsic reasons for this stabilisation¹. However, the synthetic applications in organic chemistry of this typical property, curiously, are still very rare²⁻³. Particularly, while the temporary complexation of an organic substrate creates a third dimension in the coordinated molecule and may be used to induce new stereospecific reactions on the ligands⁴, no example of such an approach taking advantage of the amplified stabilization of the α -carbenium ions in complexes has so far been reported. We show here, in several examples selected from the (arene)Cr(CO)₃ series, that the total control of the stereochemistry of nucleophilic attack (SN₁ type reaction) may be obtained in this way.

It is well documented that, among the two possible diastereoisomers "endo" and "exo", only the "cis" 1-(indanol)- or (1-tetralol)Cr(CO)₃ ("endo") is easily accessible in the pure state, either by direct condensation of 1-indanol or 1-tetralol with Cr(CO)₆ or by reduction with metal hydrides of (1-indanone)- or (1-tetralone)Cr(CO)₃⁵. A similar behavior has been recognized in the case of (1-methoxy indane)Cr(CO)₃; condensation of the free ligand with Cr(CO)₆ is kinetically controlled and favours the preparation of the "endo" isomer⁶. Now, the "exo" diastereoisomer is easily attainable with a high purity by total inversion of the stereochemistry of the carbon atom α to the (arene)Cr(CO)₃ entity. The procedure is as follows.



Scheme 1



Scheme 2

The carbenium ion derived from the "endo" (1-indanol)Cr(CO)₃ 1 (racemic : m.p. 105°) was generated by addition at -30°C under nitrogen of a degassed solution of the alcohol 1 in CH₂Cl₂ to a mixture (1:1 vol.) of concentrated H₂SO₄ and CH₂Cl₂. The deep blue solution was rapidly poured into an ice-water mixture leading to the "exo" (1-indanol-Cr(CO)₃ 2 (racemic : m.p. 89° ; nmr (CDCl₃) : CH, δ : 5.22 (m) ; OH, δ : 2.24 (m)) without any trace of the starting alcohol 1 and with an overall yield of 55 % (isolated product). The structure of 2 has been ascertained by comparison with an authentic sample^{5d}. The same reaction has been carried out in the optically active series. Starting from the optically pure 1R indanol 1 (m.p. 110° ; |α_D²² = + 60°9, CHCl₃⁷) the "exo" isomer 2 (m.p. 94° ; |α_D²² = + 81°3) was obtained. The oxidative decomposition of 2 gave rise to the free ligand 4 (|α_D²² = + 31° ; m.p. 72°) of 1S absolute configuration with an optical purity superior to 90 %⁸ (scheme 1).

Concerning the preparation of the "exo" ethers, a slight modification of the procedure, avoiding the separate preparation of the carbenium ion, improved the yields (75 %). For example, "exo" (1-methoxy indane)Cr(CO)₃ 3 (racemic : m.p. 96° ; nmr (CDCl₃) : CH, δ : 4.62 (m) ; CH₃O, δ : 3.47 (s)) was easily prepared by adding H₂SO₄ dropwise into a methanolic solution of alcohol 1 at -15°C. In this case, the carbenium ion reacts very rapidly with methanol prior to decomposition. The preparation of "exo" (1-N-dimethylamino-indane)Cr(CO)₃ (racemic : m.p. 82° ; nmr (CDCl₃) : CH, δ : 4.21 (m) ; N(CH₃)₂, δ : 2.33 (s)) has also been possible starting from the "endo" alcohol 1. However the yields were then in the region of 25 % owing to the experimental conditions

In the following table are listed the characteristic properties of a series of optically active alicyclic alcohols and ethers prepared according to the above methods from optically pure 1R 1 and 1R 11 (m.p. 140° ; |α_D²² = -20°)⁸. The absolute configuration of the compounds given in the table are unambiguously established because nucleophilic attack on the carbenium ion complexes is stereoselective in an exo fashion ; they are those shown in scheme 1.

Products	2	3	4	5	12	13	15	16
α _D ²² (°)	+81.3	+86	31 (a)	+19.1	+123	+110	+27.9(b)	-3.5
m.p. (°)	94	77	72	oil	69	84	oil	oil
Yield (%)	55	79	75	89	49	51	67	68

(a) lit : +34°⁸ ; (b) lit : + 26°⁸.

It is remarkable that the inversions of configuration take place with a very high stereoselectivity. Thus, for example, the 1S tetralol 15 obtained by decomplexation of 12 can be considered to be optically pure ($[\alpha]_D^{22} = +27^\circ 9$, lit⁸ : $[\alpha]_D^{22} = +26^\circ 8$). In the tetralol series, the olefin complex 14 (m.p. 106° , $[\alpha]_D^{22} = -1180^\circ$) has been isolated as a side product (yield : 15 %). This dehydration reaction is amplified (yield : 46 %) in the course of the preparation of the ether 13.

The presence of an "exo" alkyl substituent on the alicyclic ring does not affect the selectivity of the reaction. Scheme 2 shows how a "trans" structure in an organic ligand 6 may be converted to "cis" configuration 9 and 10.

The indanol 6 (racemic : m.p. 84°) afforded 7 (m.p. 110° ; nmr (CDCl₃ : CH, δ : 4.92 (m) ; OH, δ : 1.97 (m) ; CH₃, δ : 11.24 (d)) and 9 (m.p. 46°) with respective yields of 85 % and 82 %, while the ethers 8 (m.p. 135° , nmr (CDCl₃) : CH, δ : 4.36 (d) ; CH₃O, δ : 3.76 (s) ; CH₃, δ : 1.27 (d)) and 10 (oil, nmr (CDCl₃) : CH, δ : 4.59 (d) ; CH₃O, δ : 3.58 (s) ; CH₃, δ : 1.18 (d)) were obtained in 80 % and 86 % yields.

We are currently undertaking further studies in this area.

Acknowledgment. We thank Dr. B.F.G. Johnson for helpful discussions and D.G.R.S.T. for financial support.

References

1. Reviews : M. Caïs, *Organometal. Chem. Rev.*, 1, 435 (1966) ; L. Haynes and R. Pettit in "Carbonium Ions", G.A. Olah and P.V.R. Schleyer, Eds, vol. 5, Wiley, N.Y. (1975).
2. For a recent review see : K.M. Nicholas, M.O. Nestle and D. Seyferth in "Transition Metal Organometallics in Organic Synthesis", H. Alper Ed., vol. 2, Academic Press (1978).
3. a. S. Top, B. Caro and G. Jaouen, *Tetrahedron Letters*, 787 (1978) ;
b. D. Seyferth, J.S. Merola and C.S. Eschbach, *J. Amer. Chem. Soc.*, 100, 4124 (1978).
4. G. Jaouen in "The Place of Transition Metals in Organic Synthesis", *Ann. N.Y. Acad. Sci.*, 295, 59 (1977).
5. a. G. Jaouen and R. Dabard, *Bull. Soc. Chim. Fr.*, 2009 (1974) ; b. G. Jaouen B. Caro and J.Y. Le Bihan, *C.R. Acad. Sci., Ser. C*, 274, 902 (1972) ;
c. W.R. Jackson and T.R.B. Mitchell, *J. Chem. Soc. (B)*, 1228 (1969) ;
d. W.R. Jackson and C.H. Mc Mullen, *J. Chem. Soc.*, 1170 (1965).
6. D.E.F. Gracey, W.R. Jackson, W.B. Jennings and T.R.B. Mitchell, *J. Chem. Soc. (B)*, 1204 (1969).
7. Specific rotations were measured in CHCl₃ using a Perkin-Elmer 241 MC polarimeter and for concentrations C = 2 or 2.5 g/l.
8. G. Jaouen and A. Meyer, *J. Amer. Chem. Soc.*, 97, 4667 (1975).

(Received in UK 2 July 1979)