Tetrahedron Letters No. 43, pp 3793 - 3796, 1974. Pergamon Press. Printed in Great Britain.

REGENERATION OF ORGANIC LIGANDS FROM Rh(III)-COMPLEXES BY CARBON MONOXIDE IN ALCOHOLS

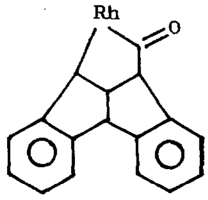
Brian F.G. Johnson, Jack Lewis* and S.W. Tam

University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K.

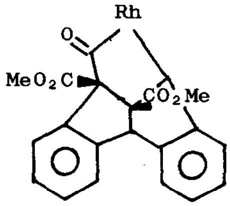
(Received in UK 9 September 1974; accepted for publication 18 September 1974)

TRANSITION metal catalysed rearrangements of cyclopropane systems is a subject of current interest[1]. Recently, Gassman[2] and Dauben[3] independently demonstrated that tricyclo$[4.1.0.0^{2,7}]$ heptanes in the presence of $[Rh(CO)_2Cl]_2$ as catalyst yielded different products depending on the pH of the methanolic solutions. Furthermore, the number and positions of the methyl substituents governed the reaction course and gave products with basically different skeletons[2,3].

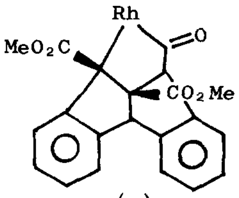
We have shown previously[4] that whilst the parent complex (1) does not react with CO in CH_2Cl_2 or $CHCl_3$, a mixture of (2) and (3) gave the free organic ligand (4) and $[Rh(CO)_2Cl]_2$ in almost quantitative yields.



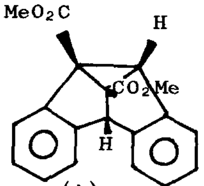
(1)



(2)



(3)



(4)

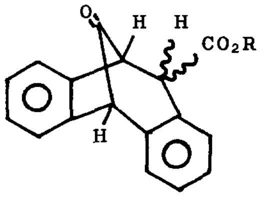
In order to gain further insights into the effects of the two carbomethoxy substituents in these complexes, we have extended our studies to the reactions with CO in alcohols. Table I summarizes the conditions and products of these reactions.

In a typical reaction, a suspension of (1) (30 mg) in MeOH (20 ml) was shaken in an autoclave for 3 days. Dark brown crystals of $Rh_6(CO)_{16}$ were separated and the filtrate, after concentration, was chromatographed (TLC, silica gel; CH_2Cl_2) to give one major and traces of two minor products. The major

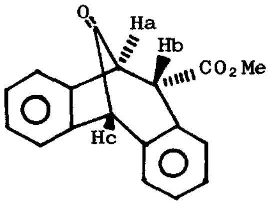
TABLE I

Compounds	Solvent	Temp.	Pressure	Time	Organic Products (yield %)
(1)	MeOH	room	1 atm.	7 days	(5)(51%)
(1)	MeOH	40°	100 "	3 "	(5)(46%)
(1)	EtOH	room	1 "	10 "	(6)(traces)
(1)	EtOH	40°	100 "	6 "	(6)(56%)
(2) + (3)	$CHCl_3$	room	1 "	21 hrs.	(4)(>90%)[4]
(2) + (3)	MeOH	40°	100 "	60 "	(4)(45%); (7)(overall 30%)
(2) + (3)	EtOH	40°	90 "	60 "	(8)(28%); (9)(30%); (4)(10%); (10)(traces)

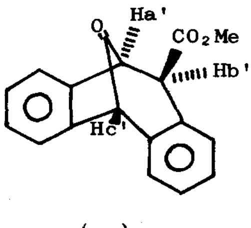
component gave (5) as colourless needles (ether) (51%; m.p. 152-3°). Found : C, 77.58; H, 5.27 and no residue. $C_{18}H_{14}O_3$ requires C,77.68; H,5.07%, ν_{max} (CCl_4) 1720 and 1745 cm^{-1} (>C=O) are in agreement with that of some bicyclo-[3.2.1]octan-8-one ester derivatives[5]. MS registered molecular ion at m/e 278 ($C_{18}H_{14}O_3$) and fragment ions at m/e 263[M-Me]; 250[M$\overset{*}{-}$CO, m* 224.8]; 247[M-OMe]; 246[M-MeOH]; 219[247$\overset{*}{-}$CO, m* 149.2]; 218[246$\overset{*}{-}$CO, m* 193.1]; 191[219$\overset{*}{-}$CO, m* 166.6]. These data are consistent with the presence of a ketonic >C=O and a carbomethoxy groups in (5).



(5), R = Me
(6), R = Et



(5a)

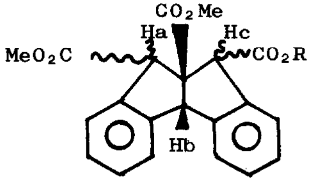


(5b)

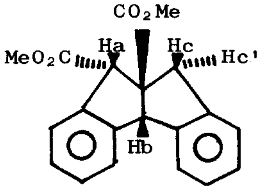
The signals of its NMR spectrum (CCl_4) were in accord with the structures of two diastereomers in a 1:1 ratio: τ, 2.2-2.8 (aromatic, m, 16 H); 5.01 (H_a, $H_{a'}$, d, J = 7.2Hz, 2 H); 5.38 (H_c or $H_{c'}$, s, 1 H); 5.48 (H_c or $H_{c'}$, s, 1 H); 6.08 (H_b or $H_{b'}$, d, J = 7.2Hz, 1 H); 6.19 (H_b or $H_{b'}$, d, J = 7.2Hz, 1 H) and 6.30 (ester OMe, s, 6 H). Decoupling experiments confirmed the above assignments In the presence of the shift reagent, $Eu(fod)_3$, decoupling experiments gave similar results. H_c and $H_{c'}$ suffered the largest down-field shift, followed by H_b and $H_{b'}$; H_a and $H_{a'}$ were least affected. The extent to which each set of protons in the two diastereomers were shifted were almost identical.

Reaction of (1) in EtOH gave the corresponding ethyl ester (6) as colourless plates (56%; m.p. 158-9°). Found: C, 77.92; H, 5.43. $C_{19}H_{16}O_3$ requires C, 78.06; H, 5.52%. MS showed molecular ion at m/e 292 ($C_{19}H_{16}O_3$). Its IR and NMR spectra were in full accord with structure (6) which again was a mixture of two diastereomers in a 1:1 ratio. Under these reaction conditions, it is not surprising that racemerization had taken place yielding an equilibrium mixture of two diastereomers.

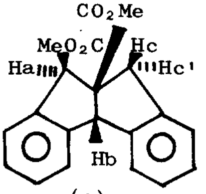
In contrast to the reaction between (2) and (3) with CO in $CHCl_3$, which gave almost quantitative yield of the free organic ligand (4)[4], the same reaction in MeOH gave, in addition to (4), a mixture of two diastereomers (7) in the ratio of ca 3:1. MS of the mixture (7) showed molecular ion at m/e 380 and fragment ions at m/e 349[M-OMe]; 348[M-MeOH]; 321[349-CO]; 320[348-CO]; 288[320-MeOH]; 260[288-CO]. Although the separation of these two diastereomers have not yet been achieved, its NMR spectrum as summarized in Table II, allowed one to assign the signals to each isomer. However, the exact stereochemistry of these diastereomers were undetermined.



(7) R = Mr
(10) R = Et



(8)



(9)

TABLE II

Chemical shifts (τ) of protons in compounds (7)-(9) in $CDCl_3$

Compounds	Ester OMe	H_a	H_b	H_c (and $H_{c'}$)
(7)(major)	6.27; 6.30; 6.37	5.10 or 5.25	4.98	5.10 or 5.25
(7)(minor)	6.18; 6.24; 6.52	5.19	4.90	5.19
(8)	6.22; 6.27	5.13	5.10	6.73 (q, J=16Hz; 2H)
(9)	6.34; 6.38	5.77	4.86	6.61 (q, J=17Hz; 2H)

Reaction of (2) and (3) in EtOH gave a mixture from which (8) was separated (TLC, silica gel; CH_2Cl_2) as colourless needles (pet. ether) (32%; m.p. 116-8°). Found: C, 74.49; H, 5.42. $C_{20}H_{18}O_4$ requires C, 74.52; H, 5.63%. $\nu_{max}(CH_2Cl_2)$ 1740-1700 cm^{-1} (broad, ester C = O); MS showed molecular ion at <u>m</u>/<u>e</u> 322 ($C_{20}H_{18}O_4$) and fragment ions at <u>m</u>/<u>e</u> 290[$\overset{*}{M}$-MeOH, m* 261.2]; 262[$29\overset{*}{0}$-CO, m* 236.7]; 247[262-Me]; 231[262-OMe]; 230[262-MeOH]; 219[247-CO]; 203[231-CO] 202[230-CO].

Its stereoisomer (9) was obtained from the fraction also containing (4). MS showed two distinct ions at <u>m</u>/<u>e</u> 322 and 320 in the highest mass region. Its NMR spectrum readily allowed one to recognise the two sets of signals. The ratio of (9):(4) was <u>ca</u> 3:1. In view of the similar properties between these two compounds on TLC and the marked difference in chemical shifts between H_a and H_b in (9), it is tempting to suggest that the stereochemistry of the two ester groups in (9) may probably be <u>cis</u>; and hence those in (8) be <u>trans</u>.

The third fraction gave traces amount of a compound (or a mixture of diastereomers) whose structure was consistent with (10) according to its MS: molecular ion at <u>m</u>/<u>e</u> 394 ($C_{23}H_{22}O_6$) and fragment ions at 362[M-MeOH]; 348 [M-EtOH]; 334[362-CO]; 320[348-CO]. However, insufficient material prevented further detailed analysis.

<u>ACKNOWLEDGEMENTS</u> :- We thank Johnson Matthey Co. Ltd. for a loan of rhodium chloride. One of us (S.W.T.) acknowledges leave of absence from the Chinese University of Hong Kong and the award of a Senior Fellowship by the Inter-University Council.

<u>REFERENCES</u>

1. T.J. Katz and S.A. Cerefice, <u>J.Am.Chem.Soc</u>., <u>93</u>, 1049 (1971); and references 1-6 cited in.
2. P.G. Gassman and R.R. Reitz, <u>J.Am.Chem.Soc</u>., <u>95</u>, 3057 (1973).
3. W.G. Dauben, A.J. Kielbania, and K.N. Raymond, <u>J.Am.Chem.Soc</u>., <u>95</u>, 7166 (1973).
4. B.F.G. Johnson, J. Lewis and S.W. Tam, <u>J.C.S. Dalton</u>, Submitted.
5. R.P. Nelson, J.M. McEuen, and R.C. Lawton, <u>J.Org.Chem</u>., <u>34</u>, 1225, (1969).