Journal of Organometallic Chemistry, 236 (1982) 95—100
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

RADICAL HYDROFORMYLATION AND HYDROGENATION OF CYCLOPROPENES WITH $HCo(CO)_4$ AND $HMn(CO)_5$

THEODORE E. NALESNIK, JOHN H. FREUDENBERGER and MILTON ORCHIN
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221 (U.S.A.)

(Received January 20th, 1982; in revised form April 15th, 1982)

Summary

The results of a study of the reactions of $HCo(CO)_4$ and $HMn(CO)_5$ with a variety of substituted cyclopropenes are consistent with the formation of intermediate caged radical pairs; recombination in the cage of the radical pair leads to hydroformylation, and cage escape leads to hydrogenation. Steric factors play an important role in determining rates as well as the stereochemistry of the products.

Introduction

The observations of CIDNP effects in the stoichiometric hydrogenation of α-methylstyrene with $HMn(CO)_5$ [1], the stoichiometric hydroformylation of 3,3-dimethyl-1,2-diphenylcyclopropene with $HMn(CO)_5$ [2] and the stoichiometric hydrogenation of 1,1-diphenylethylene with $HCo(CO)_4$ [3] clearly demonstrate that such reactions proceed via a radical pair mechanism. As has been pointed out earlier [4], the radical pair mechanism which prevails in these cases is completely different than the mechanism for the well-studied stoichiometric hydroformylation of 1-alkenes with $HCo(CO)_4$.

In view of the propensity of cyclopropenes to form radical pairs [2] we have now extended our studies to the reactions of a series of such compounds with both $HCo(CO)_4$ and $HMn(CO)_5$. The objectives of such a study were to secure information on rates, competitive partitioning between hydroformylation and hydrogenation, stereochemical control, and to confirm the observed parallelism between $HCo(CO)_4$ and $HMn(CO)_5$ reactions with particular substrates [5].

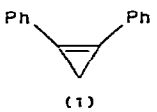
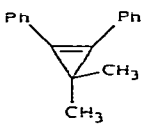
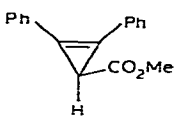
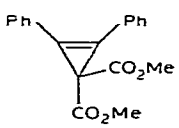
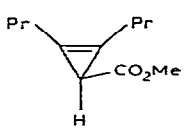
Results and discussion

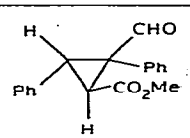
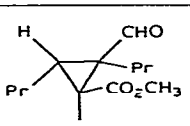
The cyclopropenes used in this study and the results obtained with them are summarized in Table 1. Previous careful kinetic studies [5] have shown that the

0022-328X/82/0000—0000/$02.75

TABLE 1

REACTIONS OF CYCLOPROPENES WITH $HCo(CO)_4$ AND $HMn(CO)_5$

Cyclopropene	$HCo(CO)_4$			$HMn(CO)_5$		
	Reaction time Temperature (°C)	Ald (%) (*cis/trans*)	Hyd (%) (*cis/trans*)	Reaction time Temperature (°C)	Ald (%) (*cis/trans*)	Hyd (%) (*cis/trans*)
 (1)	3 min 25	34 (92/8)	65	10 min 25	39 (94/6)	59
 (2)	30 min 25	18—22 (94/6)	78 (88/12)	2—4 h 60	37 (88/12)	63 (88/12)
 (3)	3 h 25	18—22 (97/3) [a]	64 (88/12)	24 h 60	0	100 (88/12)
 (4)	3 h (60%) 25	0	100 (100% *cis*)	24 h (75%) 60	0	100 (100% *cis*)
 (5)	24 h 25	57 100 [b]	37	NO Rxn.		

[a] 97%  see ref. [15]; 3% unidentified. [b] Assumed to be  .

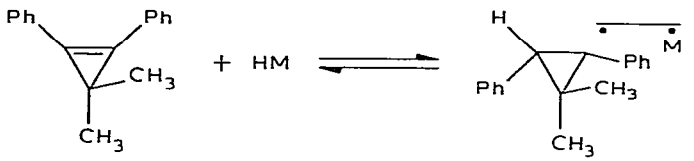
rate of reaction of $HCo(CO)_4$ and $DCo(CO)_4$ with a variety of aromatic conjugated olefins parallels the rate of reaction of these olefins with $HMn(CO)_5$ and $DMn(CO)_5$; however the reactions with cobalt are two or three orders of magnitude faster than those with manganese. Although our present rate data are only qualitative, Table 1 shows a similar parallelism.

The compounds shown in Table 1 are listed in decreasing order of reactivity. This order is best explained on the basis of steric effects of the cyclopropene as well as on the stability of the intermediate radical formed as a result of hydrogen abstraction from the metal hydride HM (M = $Co(CO)_4$ or $Mn(CO)_5$).

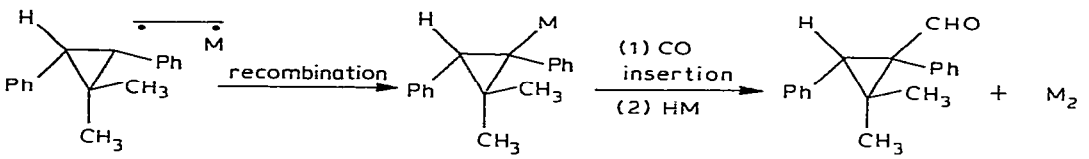
As we have noted in an earlier paper [2] hydroformylation with HM proceeds in the radical cage via recombination. After recombination, CO insertion

followed by reaction with a second mol of HM yields aldehyde. Hydrogenation occurs when the radical pair escapes the cage and the organic radical then abstracts hydrogen from another mol of HM. The partitioning between hydroformylation and hydrogenation is thus determined by the competition between recombination inside the cage and escape from it, Scheme 1, (a) and (b) respectively.

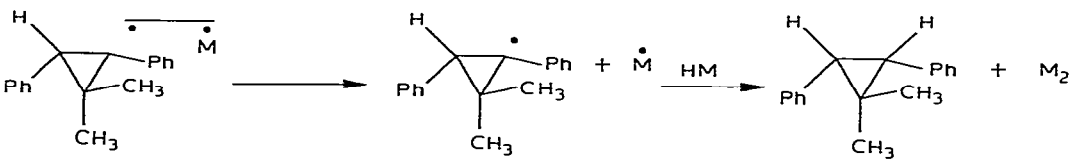
SCHEME 1



(a) Hydroformylation



(b) Hydrogenation



(M = $Co(CO)_4$, $Mn(CO)_5$)

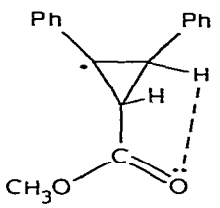
Radicals from cyclopropenes tend to be rather more pyramidal rather than planar at the radical carbon center [6] and pyramidal carbon, because of its higher directional character, probably favors recombination (aldehyde). This probably accounts for the successful hydroformylation of 1 and 2 with $HMn(CO)_5$ in contrast to the exclusive hydrogenation of, e.g., α-methylstyrene [1] which forms a more planar carbon radical center. The failure to obtain hydroformylation with 3 and 4 with $HMn(CO)_5$ in contrast to hydroformylation of 3 with $HCo(CO)_4$ may result from the resistance to recombination because of the greater steric bulk of $Mn(CO)_5$ as compared to $Co(CO)_4$.

The behavior of 5 requires comment. The double bond of 5 is probably more sterically accessible to reaction than the double bond in the other cyclopropenes listed in Table 1; however 5 reacts more slowly. If the radical formed by hydrogen abstraction were the intermediate, we would not expect it to be as reso-

nance-stabilized as that derived from the phenyl substituted cyclopropenes.

All the cyclopropenes react more slowly with $HMn(CO)_5$ than with $HCo(CO)_4$; the difference in rate is attributable to the smaller bond dissociation energy of H—Co as compared to H—Mn [5,7].

The configuration of the products, in the cases where the stereochemistry was ascertained, is also shown in Table 1. Of the four possible racemic aldehydes that may be formed from 3 by hydroformylation, the one shown is essentially the only one generated. Because the aldehyde is formed by radical recombination in the cage, it is to be expected that *cis*-aldehyde would predominate but the fact that the more hindered face of 3 is attacked is unexpected. It is possible that such attack is favored because of enhanced stability of the intermediate radical due to hydrogen bonding with the carbomethoxy group on the same face as the hydrogen to give a structure such as 6.



(6)

Alternatively, the undissociated $HCo(CO)_4$, prior to attack, may prefer to contact the cyclopropene on the same face as the carbomethoxy group because of hydrogen bonding.

Table 1 shows that a small quantity of *trans*-aldehyde is usually formed. It should be appreciated that its formation via geminate radical pair recombination in the cage requires inversion at the pyramidal trigonal carbon as well as a 180° rotation of the cyclopropyl group around an axis in the plane of the cyclopropyl group. Such rotation and inversion have been shown to be possible for cyclopropyl radicals [8,9]. The large preponderance of the *cis*-aldehyde indicates, as expected, that recombination before inversion-rotation is favored.

Experimental

1,2-Diphenylcyclopropene (1), was prepared from diphenylcyclopropenyl perchlorate [10] by the literature method [11].

Reaction of 1 *with* $HCo(CO)_4$

Pure 1 (0.559 g) was added under CO to 50 ml of 0.13 *M* $HCo(CO)_4$ in pentane. After 10 min the solution was evaporated in a stream of CO, the residue dissolved in hexane, and the components separated on an 8 inch silica gel column. ^{1}H NMR analysis indicated a 64.8% yield of hydrogenated product and a 34.2%yield of aldehydes. The hydrogenation products could not be successfully separated on a silica gel column and GC analysis was useless because of isomerization at the GC inport temperatures. ^{1}H NMR of the hydroformylated product showed two aldehyde peaks, one at δ 8.95 (8%, *trans*). The *trans*

isomer was not isolated in pure form, but the *cis* isomer was recrystallized from hot hexane: m.p.: 69.5—70.5°C, ^{1}H NMR ($CDCl_3$) δ 9.58 (s,1,aldehyde), δ 6.6—7.5 (m,10,phenyls), 3.01 (t,1,benzyl), 2.15 (t,1,methine), 2.05 (t,1,methine). IR ($CHCl_3$) 3037m, 2937w, 2851w, 2761w, 2721w, 1711vs, 1220s. Anal. ($C_{16}H_{14}O$)C,H.

Reaction of **1** *with* $HMn(CO)_5$

A mixture of 0.250 g **1** and 0.556 g $HMn(CO)_5$ were dissolved in 15 ml pentane under CO and allowed to stir for 24 h at room temperature. Separation on a silica gel column gave, after removal of the first fraction containing $Mn_2(CO)_{10}$, 59% of hydrogenated product and 39% of hydroformylated product, consisting of 6% *trans* and 94% *cis* aldehyde (^{1}H NMR).

Methyl 1,2-di-n-propyl-3-cyclopropenecarboxylate (**5**), was prepared from the corresponding acid [12] with diazomethane [13].

Reaction of **5** *with* $HCo(CO)_4$

The reaction was carried out in the same manner as with **1**. The products were separated on a silica gel column using hexanes as the eluant to separate the $Co_2(CO)_8$ and then 1/1 hexane/$CHCl_3$ to separate hydrogenated and hydroformylated products.

The hydrogenated isomers (36% yield) were not separated. Only one hydroformylated product was found (57% yield). In analogy to the products from **3** this is presumed to be methyl *t,t*-2,3-di-n-propyl-*c*-2-formylcyclopropane-*r*-1-carboxylate: oil; ^{1}H NMR δ 9.30 (s,1,aldehyde), 3.67 (s,3,methoxy), 2.38—2.12 (m,1,cyclopropyl), 1.83 (d,1,cyclopropyl), 1.75—1.18 (m,8,ethylene), 1.18—0.72 (m,6,methyl); IR; 2967s, 2877s, 1734vs, 1706vs, 1455m, 1175s, 917m, 736s. On standing, the aldehyde was spontaneously oxidized to the corresponding acid. Anal. ($C_{12}H_{20}O_4$)C,H.

3,3-Dimethyl-1,2-diphenylcyclopropene (**2**) was prepared according to the literature [14]. It was then treated respectively with $HCo(CO)_4$ and $HMn(CO)_5$ in the same manner as with **1**. The yields shown in Table 1 were virtually the same under either a CO or an argon atmosphere. The physical and spectral data of the products have been previously reported [2].

Methyl 1,2-diphenyl-3-cyclopropenecarboxylate (**3**), was prepared and treated as previously described [15]. The yields obtained were identical with those previously reported [15] and did not change when the reaction was performed under N_2 and in the presence of two equivalents of *p*-methoxybenzonitrile [16]. After filtering the major hydroformylated product (*cis*-addition, *cis* to the carbomethoxy group), an analysis of the remaining products, more exhaustively carried out than previously [15], revealed a very small amount of another aldehyde with a ^{1}H NMR ($CDCl_3$) shift 2 Hz upfield of the major aldehyde product. This other aldehyde comprised about 3% of the total aldehyde yield, and was present in quantities too small for further characterization.

Dimethyl 1,2-diphenylcyclopropene-3,3-dicarboxylate (**4**), was prepared according to the literature procedures [17]. It was treated with $HCo(CO)_4$ in a similar manner as **1**, except CH_2Cl_2 was used as the solvent instead of pentane. After the reaction was allowed to proceed for 3 h, 1.0 ml of ethylenediamine was added. After several washings with H_2O, the CH_2Cl_2 solution was dried and

evaporated. A mixture of 60% hydrogenated product and 40% starting material remained; no aldehyde could be detected. The product consisted solely of *cis* isomer, dimethyl *c*-2,3-diphenylcyclopropane-1,1-dicarboxylate: m.p. 145—146°C; ^{1}H NMR ($CDCl_3$) δ 7.16 (m,10,phenyl), 3.80 (s,3,methoxy), 3.40 (s,3, methoxy), 3.38 (s,2,methine); IR ($CHCl_3$) 3020w, 1735vs, 1600w, 1495m, 1436s, 1330m, 1255vs, 1215vs, 1155m, 1090m, cm^{-1}. Anal. ($C_{19}H_{18}O_4$)C,H. Authentic *trans* isomer, dimethyl *t*-2,3-diphenylcyclopropane-1,1-dicarboxylate was prepared for comparison purposes. In a 25 ml single-neck flask equipped with a magnetic stirring bar and an addition funnel was placed 7.0 g (0.039 mol) of *trans*-stilbene and 0.5 g Cu powder. After flushing with N_2, the flask was heated to 135°C in an oil bath, and 3.0 g (0.109 mol) of diazodimethylmalonate [18] was added dropwise over a 3 h period. After 45 min of additional heating, the product was dissolved in 35 ml CH_2Cl_2, filtered, and cooled in a freezer to precipitate unconverted *trans*-stilbene (3.8 g). Column chromatography using 1/1 $CHCl_3$ to hexane on a 1" × 10" column of silica gel gave, as the second band (the first being *trans*-stilbene), 1.46 g of product. Recrystallization from hexane yielded pure colorless crystals of product: m.p. 67.5—69.5°C; ^{1}H NMR ($CDCl_3$) δ 7.27 (s,10,phenyl), 3.82 (s,6,methoxy), 3.42 (s,2,methine); IR ($CHCl_3$), 2950m, 1735vs, 1595w, 1500s, 1435vs, 1300vs, 1220vs, 1120vs cm^{-1}. Anal. ($C_{19}H_{18}O_4$)C,H.

Acknowledgement

We wish to thank The Standard Oil Co. of Ohio and the Procter and Gamble Co. for fellowship support.

References

1 R.L. Sweany and J. Halpern, J. Amer. Chem. Soc., 99 (1977) 8335.
2 T.E. Nalesnik and M. Orchin, J. Organometal. Chem., 222 (1981) C5.
3 T.E. Nalesnik and M. Orchin, Organometallics, 1 (1982) 222.
4 J.A. Roth and M. Orchin, J. Organometal. Chem., 172 (1971) 299.
5 T.E. Nalesnik, J.H. Freudenberger and M. Orchin, J. Mol. Cat., 16 (1982) 43.
6 T. Kawamura, M. Tsumura, Y. Yokamichi and T. Yonezawa, J. Amer. Chem. Soc., 99 (1977) 8251.
7 T.E. Nalesnik, Ph.D. Thesis, University of Cincinnati (1981).
8 H.M. Walborsky and J. Chen, J. Amer. Chem. Soc., 93 (1971) 671.
9 F.D. Greene, M.A. Berwick and T.C. Stowell, J. Am. Chem. Soc., 92 (1970) 867.
10 D.G. Farnum and M. Burr, J. Am. Chem. Soc., 82 (1960) 2651.
11 D.T. Longone and D.M. Stehouwer, Tetrahedron Letters, 13 (1970) 1017.
12 R. Breslow, H. Hover and H.W. Chang, J. Am. Chem. Soc., 84 (1962) 3172.
13 I.A. D'yakonov and R.R. Kostikov, Zh. Organ. Khim., 2(5) (1966) 823.
14 L.E. Friedrich and R.A. Fiato, Syn., (1973) 611.
15 T.E. Nalesnik, J.G. Fish, S.W. Horgan and M. Orchin, J. Org. Chem., 46 (1981) 1987.
16 L. Roos and M. Orchin, J. Org. Chem., 31 (1966) 3015.
17 R. Breslow, R. Winter and M. Battiste, J. Org. Chem., 24 (1959) 415.
18 B.W. Peace, F. Carman and D.S. Wulfman, Syn., (1971) 658.