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OLEFIN REACTIONS WITH $HMn(CO)_5$: PRODUCT SELECTIVITY BY MICELLE SEQUESTERING

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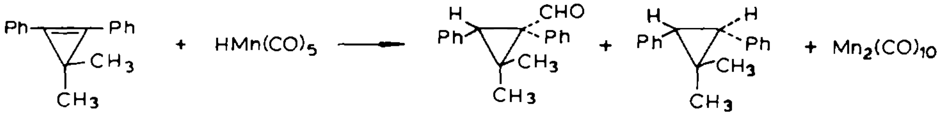
Summary

The reaction of $HMn(CO)_5$ with certain cyclopropenes when carried out in a detergent medium gives a different mixture of hydroformylated and hydrogenated products than is obtained when the same reaction is carried out in a homogeneous medium. These results are consistent with the intermediacy of caged geminate radical pairs whose escape from the cage is retarded by micelle sequestering.

Introduction

We reported earlier [1] on the first example of the stoichiometric hydroformylation of an olefin using $HMn(CO)_5$ (eq.1). When the course of this reaction was



(1)

(1) (2)(37%) (3)(63%)

monitored by ^1H NMR, a CIDNP effect was observed which was attributed to the formation of geminate radical pair **4**. Diffusion of **4** out of the solvent cage to give the free radicals was assumed to lead to the hydrogenated product **3** (CIDNP, emission) formed in 53% yield while combination inside the cage (CIDNP, enchanced absorption) gave **5**, the σ-bonded cyclopropylmanganese pentacarbonyl which reacted further to produce aldehyde **2** obtained in 27% yield (Scheme 1).

In searching for ways to modify the partitioning of **4** between escape and combination, it occurred to us to apply the elegant technique described [2] for enhancing selectivity of radical reactions by using detergent solutions. Thus the photolytic decomposition of unsymmetrical dibenzyl ketones R^1COR^2 when conducted in homogeneous solution gave the product distribution consisting of R^1R^1, (25%), R^2R^2 (25%) and R^1R^2 (50%) expected by escape of the initially formed radical

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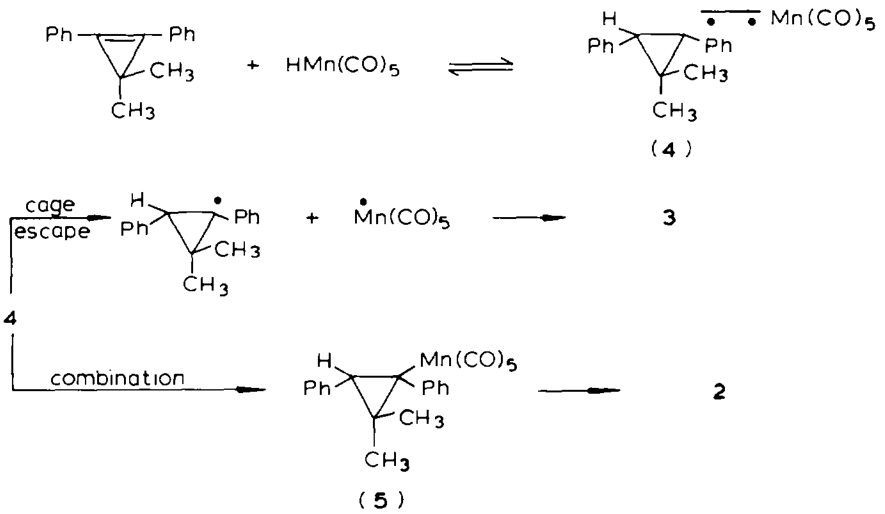
SCHEME 1



pair out of the cage, followed by statistical combination of the free radicals. However, trapping the radical pair inside the micelles created by the detergent led to almost 100% R^1R^2 the product of combination before escape. Were this general concept to be applied to our reaction (eq. 1) it might be possible to increase the proportion of aldehyde, **2**, (the ultimate product from combination) at the expense of the hydrogenated product **3**. We accordingly conducted such experiments with the results discussed below.

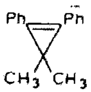
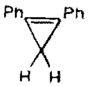
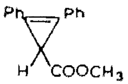
Results and discussion

In order for detergents to aggregate and form micelles the concentration of the detergent must exceed the critical micelle concentration (cmc). We have used two detergents: sodium 10-undecenoate (NaUN) at 0.2 *M* or 0.4 *M* concentration and sodium dodecyl sulfate (sodium lauryl sulfate, NaLS) at 0.4 *M*. These concentrations are well above the cmc [3].

Table 1 shows our preliminary results. All the homogeneous reactions have been reported previously [4]. It is clear that carrying out the reactions with **1** and **6** in the detergent medium leads to a substantial increase in the aldehydes at the expense of the hydrogenated products, in satisfying accordance with our expectations. It is of course possible that the difference in product composition may be due to reasons other than micelle sequestering, for example, the effect of solvent on the rate of rearrangement from alkyl- to acyl-manganese. However kinetic studies on hydrocarbon-aldehyde partitioning with styrene in the reaction with iron carbonyl hydride in a mixed phase system [5] which is a good model for our system indicated that the rate of such rearrangement was not controlling. Compounds **7** and **8**, neither of which gave any aldehyde in homogeneous solution, remained essentially unreacted in the presence of the detergent even though the detergent solutions appeared to be clear and colorless. Both **7** and **8** are probably considerably more polar than **1** and **6** and both react considerably slower with HMn(CO)$_5$ in pentane or hexanes solution. It has been shown [6] that α-methylstyrene reacts with HMn(CO)$_5$ to form the

TABLE I

COMPARISON OF $HMn(CO)_5$ REACTIONS IN HOMOGENEOUS AND DETERGENT MEDIA

Reactant	Homogeneous (pentane or hexanes)			Micellar[a]			
	Conditions (°C/h)	Aldehyde (%)	Hydride (%)	Conditions (50°C)	Aldehyde (%)	Hydride (%)	Yield[b] (%)
 1	60/3–4	37 (88/12)[e]	63 (88/12)[e]	NaUN[c] 0.4 *M* 250ml 15 h	92 (85/15)[e]	8 (~ 100 *cis*)	98
				NaLS[d] 0.2 *M* 250 ml 14 h	93 (85/15)[e]	7 (~ 100 *cis*)	98
 6	25/24	39 (94/6)[e]	59	NaUN[c] 0.2 *M* 500 ml 10 h	93 (79/21)[e]	7 (~ 100 *cis*)	86
				NaLS[d] 0.2 *M* 14 h 250 ml	89 (79/21)[e]	11 (~ 100 *cis*)	89
 7	60/24	0	100 (88/12)[e]	NaUN[c] 0.4 *M* 250 ml 16 h	No reaction		
$Ph_2C{=}CH_2$ 8	25/15 (conversion 30%)	0	100	NaUN[d] 0.4 *M* 250 ml 22 h	No reaction		

[a] 0.5 mmol olefin, 2 mmol $HMn(CO)_5$, conversion 100% unless otherwise noted. [b] Sum of aldehyde and cyclopropane. [c] $CH_2{=}CH(CH_2)_8COONa$. [d] $CH_3(CH_2)_{11}OSO_3Na$. [e] (*cis*/*trans*).

geminate radical pair but no cage combination product was isolated. The radical pair either reverted to the reactants or escaped the cage, the rates of the two processes being about equal. It would be expected that a bulkier α-substituted styrene such as **8** would be even less prone to form the combination product and since escape is retarded by micelle sequestering, the most probable fate of the radical pair, if it formed, would be reversion to reactants, and eventually $HMn(CO)_5$ decomposition. It is not certain at this time exactly why these compounds failed to react (or immeasurably slowly) in the presence of detergent.

The *cis/trans* ratios of both hydroformylated and hydrogenated product are of interest. It is reasonable to assume that geminate radical pair **4** has the *cis* configuration. In order to obtain *trans* product, both inversion at the cyclopropyl radical center as well as a 180° rotation of the cyclopropyl ring around an axis in the plane of the ring must occur. Such inversion–rotation has been previously reported for cyclopropyl radicals [7]. It will be noted from Table 1 that the aldehyde product from both **1** and **6** in the detergent medium consisted of a greater proportion of the *trans*-isomer compared to the reaction in homogeneous media. On the other hand the hydrogenated product from the detergent experiments with the two compounds was practically all *cis*. The total quantities involved were very small and analyses by ^1H NMR were probably accurate to $\pm 5\%$. Possibly the second mole of $HMn(CO)_5$ which reacts with the cyclopropyl radical as it leaves the cage is in close proximity to the radical and traps it immediately. Also, although most trigonal carbons have a planar configuration a cyclopropyl carbon radical center is assumed to be more pyramidal [7]. Further experiments will hopefully help to resolve some of the questions suggested by the present investigation.

Experimental

Materials

1,2-Diphenylcyclopropene (**6**) [8], 3,3-dimethyl-1,2-diphenylcyclopropene (**1**) [9], and 1,2-diphenylcyclopropene-3-carboxylic acid [10] were prepared according to the literature procedures. Methyl 2,3-diphenyl-2-cyclopropene-1-carboxylate (**7**) was prepared by esterification of the acid using CH_2N_2. $HMn(CO)_5$ was prepared as reported in the literature [11].

Sodium 10-undecenoate ($CH_2{=}CH(CH_2)_8COONa$)

20 g (0.50 mol) of NaOH was dissolved in 400 ml of water. To this solution was added, 94 g (0.51 mol) of 10-undecenoic acid obtained by vacuum distillation of the commercial product (Alfa). The mixture was stirred for 1 h. The resulting solution was evaporated in a rotary evaporator in 40 ml batches. The solid was dried under vacuum. The resulting white powder was washed with hexanes until the washings were completely acid free (GLC of esterification product) and then it was dried in vacuum.

Sodium dodecyl sulfate $CH_3(CH_2)_{11}OSO_3Na$

The commercial product (Aldrich) was washed with hexanes until the washings did not contain any dodecyl alcohol, (GLC).

Hydroformylation procedure

In a typical reaction, a 300 ml three neck flask equipped with a stirring bar and septum was purged with CO. The detergent (0.1 mol) and 250 ml of water (bubbled with argon for 24 h) were added to the flask immersed in a water-bath (50°C). After 1 h stirring, olefin (0.5 mmol) was added to the flask and the solution was stirred for 2 h at 50°C under CO whereupon 2 mmol of $HMn(CO)_5$ was injected into the flask through a rubber septum. After an appropriate time, the solution was filtered in order to separate $Mn_2(CO)_{10}$ and the products were extracted with 4 × 200 ml of pentane and 4 × 200 ml of CH_2Cl_2. The extract was dried over $MgSO_4$ and the solvent was evaporated using a rotary evaporator. The residue was dissolved in a small quantity of hexanes and chromatographed on a 1/2″ × 8″ column of silica gel (230–400 mesh) using hexanes as the eluant. The first eluate consisted of a small amount of $Mn_2(CO)_{10}$ and the second fraction was hydrogenation products. Aldehydes remained near the top of the column and were eluted with $CHCl_3$.

Authentic samples of *cis*-1,2-diphenylcyclopropane and of *cis*-1,2-diphenyl-3,3-dimethylcyclopropane were prepared by the hydrogenation of the corresponding cyclopropenes **6** and **1**, respectively, using a 5% Pd/C catalyst. The reaction was carried out in pentane solvent at room temperature by treatment with H_2 for 30 min at 500 psi. Authentic *cis*-aldehydes were prepared by hydroformylation of **6** and **1** using $[RhCl(CO)_2]_2$ catalyst at 50°C and 1600 psi of CO/H_2 for 6 h. These authentic compounds were used as GLC standards.

Analyses

The ratio of hydroformylation and hydrogenation products was determined by GLC. The ratio of *cis*- and *trans*-isomers was determined by ^1H NMR. Gas chromatographic analyses were performed on a 1/4″ × 7′ copper column filled with 3% SE-30 on Chromosorb W operating at 190°C under flowing He in a F&M model 700 GLC having a katharometer detector.

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