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Preliminary communication

STOICHIOMETRIC HYDROFORMYLATION WITH $HMn(CO)_5$

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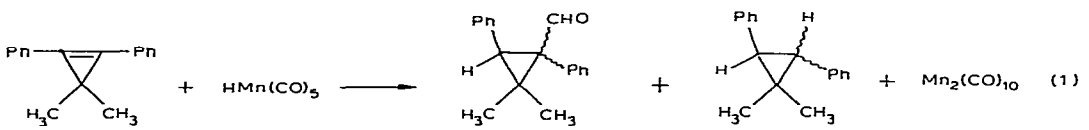
Summary

We report here the first example of a stoichiometric hydroformylation using $HMn(CO)_5$. Treatment of a hexane solution of 1,2-diphenyl-3,3-dimethylcyclopropene with $HMn(CO)_5$ at 55°C gave after 5 h a 27% yield of aldehydes, 87% *cis* and 13% *trans*. The other major products were *cis*-(87%)-, and *trans*-(13%)-1,2-diphenyl-3,3-dimethylcyclopropane. Evidence for a radical intermediate is presented.

We wish to report what we believe to be the first example of hydroformylation of an olefin using $HMn(CO)_5$ (eq. 1). The reaction was carried out in



(I) (II) (III)

hexane solution at 55°C under 1 atm CO and gave, after chromatography, the aldehydes II in about 27% yield. The hydrogenated products III were formed in about 53% yield. Both the aldehydes and the hydrogenated products were estimated to consist of about 87% *cis* and 13% *trans*. The absence of hydrogen atoms alpha to the double bond in I precludes the possibility of $HMn(CO)_5$-catalyzed isomerization.

The reaction of I with $HMn(CO)_5$ proceeds via the radical pair IV formed after abstraction of hydrogen from $HMn(CO)_5$ by I. The loss of expected (*cis*) stereospecificity in II probably arises from both rotation and inversion of the cyclopropyl radical of the geminate pair IV while still in the solvent cage [1]. Recombination of the radical pair, predominantly at the least hindered face, leads to the cyclopropylmanganese pentacarbonyls followed by CO insertion

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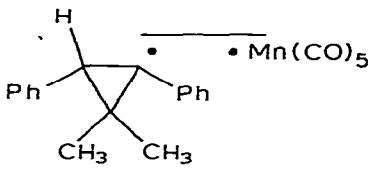

(IV)

and further reaction with a second mole of $HMn(CO)_5$ to give the aldehydes II. Diffusion of IV out of the solvent cage is followed by hydrogen abstraction from $HMn(CO)_5$ again predominantly at the least hindered face of the cyclopropyl radical to give the mixture of hydrogenated compounds. The fact that the ratio of *cis* and *trans* hydroformylation and hydrogenation products are identical, within experimental limits, may be coincidental. A further proof for a proposed radical mechanism [2] in a hydroformylation reaction comes from the observation of a CIDNP effect attributed to IV and shown in Fig. 1.

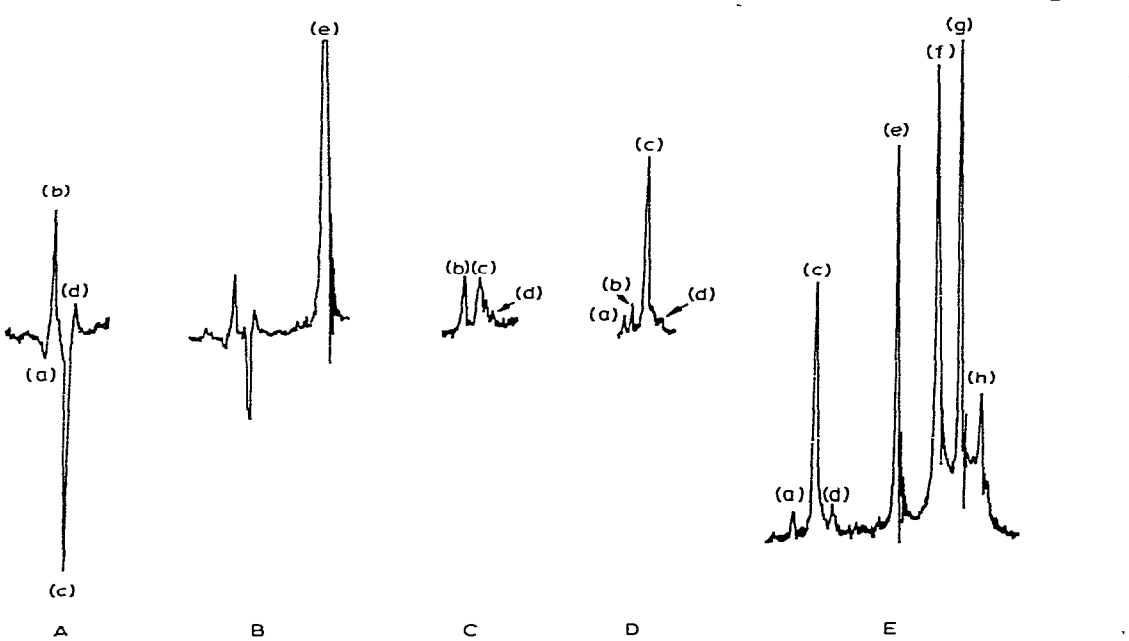

Fig. 1. ^1H NMR spectra in the 1.8—2.7 ppm range. A, first scan of reaction 1, (a) and (c) *trans*- and *cis*-cyclopropylmethine protons, respectively, (b) and (d) *cis*- and *trans*-cyclopropylmethine protons, respectively, of σ-cyclopropylmanganese carbonyl; B same as A but taken about 1 min later and (e) the *gem*-dimethyl protons of I; C, about 1 min after B, D, about 1 min after C; E, about 30 min after D, (f) and (g) *gem*-dimethyl protons of *cis*-III, (h) *gem*-dimethyl protons of *trans*-III; after long standing (b) and (d) completely disappear.

Figure 1A is the ^1H NMR spectrum obtained in the first scan of the reaction products of eq. 1. The weak emission signal (a) and the strong emission (c) correspond respectively to the *trans*- and *cis*-cyclopropylmethine protons in III. The absorption signals (b) and (d) which disappear with time, Fig. IB, IC, and ID, and are virtually gone in the spectrum of the product, Fig. IE, we tenta-

tively assign to the *cis*- and *trans*-methine protons of the σ-cyclopropylmanganese pentacarbonyl. The phase assignments are consistent with those calculated for cage recombination and cage escape products [3]. An infrared spectrum of the product obtained after 30 min reaction time showed a weak absorption at 1635 cm^{-1} which we attribute to the acylmanganese carbonyls, the precursors of aldehydes III. Stoichiometric hydroformylation using $HMn(CO)_5$ is unexpected since simple olefins are inert and phenyl-substituted ethylenes give hydrogenated products [2]. Under catalytic hydroformylation conditions, manganese reacts sluggishly [4] and is thought to be approximately 10^{-4} as reactive as cobalt [5]. We are now investigating the mechanistic details of reaction 1 as well as the corresponding reaction with $HCo(CO)_4$.

Experimental

To a solution of 1.40 g (0.0068 mol) of I [6] in 8 ml of CO-saturated hexane under CO at 55°C was added a solution of 3.75 g (0.019 mol) $HMn(CO)_5$ [7] in 6 ml of CO-saturated hexane over a 30 min period. The solution was stirred for 5 h (~50 ml CO absorbed) and the solution cooled and then chromatographed over silica gel. The first fraction, eluted with hexane, consisted of $Mn_2(CO)_{10}$ followed by III. The aldehydes II were eluted with $CHCl_3$. The *cis*-isomer of III crystallized from the concentrated hexane solution and was further purified by chromatography, m.p. 53–55°C, Anal. ($C_{17}H_{18}$) C, H. IR (thin film): 2912(s), 1588(s), 1484(vs), 1435(s), 1375(w), 1363(m), 1190(m), 1110(m), 1060(m) and 1020(m) cm^{-1}. ^1H NMR ($CHCl_3$): δ 6.80—7.35 (m, 10, phenyl), 2.25 (s, 2, methine), 1.40 (s, 3, methyl), 1.10 ppm (s, 3, methyl). The hexane mother liquor remaining after removal of *cis*-III was evaporated to dryness leaving an oil consisting principally of additional *cis* and a small quantity of *trans*-III. Anal. of mixture ($C_{17}H_{18}$) C, H. When the ^1H NMR of the pure *cis*-isomer was subtracted from the spectrum of the mixture, the difference spectrum of *trans*-III($CHCl_3$) was δ 7.18 (m, 10, phenyl), 2.40 (s, 2, methine), 0.98 ppm (s, 6, methyl). The $CHCl_3$ solution of aldehydes was chromatographed using 1/1 hexane/$CHCl_3$. The *cis*-isomer was eluted first giving a fraction that was estimated (NMR) to consist of about 90% *cis*-II. The *trans*-II was contaminated by some of the *cis*-isomer and was estimated (NMR) to consist of about 70% *trans*-II.

cis-3,3-Dimethyl-1-formyl-1,2-diphenylcyclopropane. IR (neat): 2727(w), 1705(vs), 1605(m), 1500(s), 1448(m), 1390(w), 1378(m), 1095(s), 1030(m), 985(m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.68 (s, 1, aldehyde), 6.9—7.5 (m, 10, phenyls), 3.35 (s, 1, methine), 1.48 (s, 3, methyl), 1.23 ppm (s, 3, methyl). *trans*-III.

trans-3-Dimethyl-1-formyl-1,2-diphenylcyclopropane. IR (neat): 2735(w), 1705(vs), 1605(m), 1500(s), 1448(s), 1378(w), 1105(w), 1070(w), 1030(w), 955(w), 815(w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.35 (s, 1, aldehyde), 7.39 (s, 10, phenyl), 3.2 (s, 1, methine), 1.58 (s, 3, methyl), 1.08 ppm (s, 3, methyl). Both aldehydes were oils and both were readily oxidized by air. Air oxidation of *cis*-II gave a solid acid which proved to be identical with that obtained by $KMnO_4$ oxidation of aqueous THF solution of *cis*-II. Pure 3,3-dimethyl-*cis*-1,2-

diphenylcyclopropane-1-carboxylic acid m.p. 154—156°C. Anal. ($C_{18}H_{18}O_2$) C, H. IR ($CHCl_3$ paste): 3500—2100(vs), 2610(w), 1680(vs), 1600(m), 1495(m), 1445(m), 1400(s), 1375(m), 1255(vs), 1212(vs), 1110(s), 1030(w) cm^{-1}. ^1H NMR ($CHCl_3$): δ 6.8—7.45 (m, 10, phenyls), 3.15 (s, 1, methine), 1.55 (s, 3, methyl), 1.22 ppm (s, 3, methyl). Similar oxidation of the small amount (31 mg) of *trans*-III gave a mixture of products from which no pure compound could be isolated.

Treatment of 1-octene with $HMn(CO)_5$ at 115°C for 5 h gave no reaction. CIDNP effect. In a ^1H NMR tube, containing 47 mg (0.213 mmole) of cyclopropene I, capped with a rubber septum and well flushed with argon, was injected 400 μl of dry deoxygenated benzene. The NMR tube was then placed in a ^1H NMR cavity (31°C). Amplitude on the instrument was raised until the *gem*-dimethyl proton peaks at 1.46 ppm were about two to three times the height of the recorder display. The NMR tube was then removed and 65 μl (0.48 mmole) of $HMn(CO)_5$ was injected into the tube followed by one second of vigorous shaking before immediately placing the tube back in the ^1H NMR cavity. The spectral region containing the cyclopropylmethine proton, 1.8 to 2.7 ppm, was immediately scanned. The observed CIDNP effect was present for one to two minutes after the initial injection.

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