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THE ISOMERIZATION AND HYDROGENATION OF THE MALEATE–FUMARATE SYSTEM BY COBALT HYDROCARBONYL

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SUMMARY

Treatment of dimethyl maleate with $DCo(CO)_4$ gives deuterated dimethyl fumarate and dimethyl succinate but no deuterium incorporation in the recovered maleate. The hydrogenation of dimethyl maleate to succinate proceeds via the fumarate. For the isomerization reaction, the results are best rationalized on the basis of a 1,2-*cis*-addition–elimination of $DCo(CO)_4$ while the hydrogenation probably involves 1,4-addition to the fumarate.

INTRODUCTION

The mechanism of olefin isomerization catalyzed by soluble transition metal catalyst systems continues to be a subject of considerable interest and controversy. In the case of cobalt hydrocarbonyl, $HCo(CO)_4$, there is evidence for each of at least three mechanisms: 1,3-internal hydride shift[1]; external 1,3-allylic exchange[2]; and 1,2-addition–elimination[3]. The first two of these mechanisms require a substrate with allylic hydrogen atoms. A substrate without allylic hydrogens but which in the presence of $HCo(CO)_4$ undergoes *cis–trans* isomerization would unequivocally establish the addition–elimination mechanism. We now wish to report such studies involving dimethyl maleate. In the presence of $HCo(CO)_4$, this compound not only isomerizes to the *trans* isomer but undergoes hydrogenation as well. The use of $DCo(CO)_4$ for the isomerization studies is particularly instructive.

RESULTS AND DISCUSSION

(*a*). *Isomerization*

Treatment of dimethyl maleate (2.31 mmol) with $DCo(CO)_4$* (2.26 mmol) in toluene at 26° under 1 atm. of carbon monoxide gives a mixture (VPC**) consisting of 20% dimethyl fumarate, 41% dimethyl maleate and 39% dimethyl succinate. The recovered maleate contained no deuterium; the dimethyl fumarate contained 37% mono- and 2% dideuterofumarate; and the succinate contained (undetermined)

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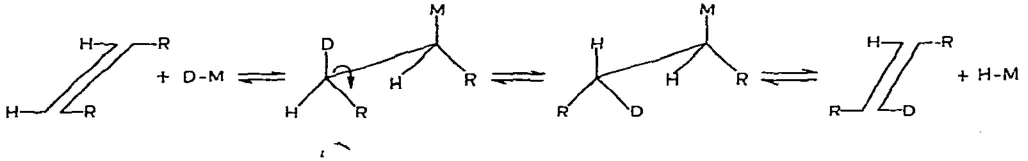
* Prepared by exchanging $HCo(CO_4)$ with D_2O, see ref. 4.

** GLC columns 13′×0.25″ copper columns packed with Ucon-50-HB-5100, 23 wt.% and $AgNO_3$, 1.5 wt%, supported on Chemisorb R. Temp. of column 180°. He carrier gas at 100 ml/min. Results in mole%.

quantities of mono-, di-, and trideutero compounds (mass spectra*).

The facile isomerization of maleate to fumarate shows that $DCo(CO)_4$ addition–elimination occurs readily under mild conditions. The complete absence of deuterium in the recovered maleate indicates that either the reaction with maleate is irreversible or that both addition and elimination must be stereospecific in the same sense. We prefer the latter explanation and believe that both addition and elimination are *cis*. With maleate, the reaction scheme (neglecting π-complexing) is:



$R = CO_2CH_3$; $M = Co(CO)_4$ or $Co(CO)_3$

(*b*). *Hydrogenation*

The reduction of olefinic bonds by $HCo(CO)_4$ has not been extensively studied because it is difficult to find substrates that are reduced rather than hydroformylated. A study of 1,2-diphenylcyclobutene[5] showed that this hydrocarbon in the presence of $HCo(CO)_4$ gives more than a 95% yield of *cis*-1,2-diphenylcyclobutane suggesting that $HCo(CO)_4$ combines with the olefin in a concerted 1,2-additon. The reduction of the carbon–carbon double bond in α,β-unsaturated aldehydes or ketones can be achieved with $HCo(CO)_4$ under stoichiometric[6] or under catalytic conditions[7]. Although the mechanism of the reduction is not known, it may very well proceed by a 1,4-addition reaction. The 1,4-addition of $HCo(CO)_4$ to butadiene and some of its derivatives has been established[8].

As indicated above, treatment of dimethyl maleate with $DCo(CO)_4$ gives appreciable quantities of dimethyl succinate. In order to investigate this reaction more thoroughly, the rate of reaction of maleate and of fumarate with $HCo(CO)_4$ was investigated.

The reaction of dimethyl maleate and $HCo(CO)_4$ (1/1) in toluene under 1 atm. of carbon monoxide gives the interesting results shown in Fig. 1. There is an induction

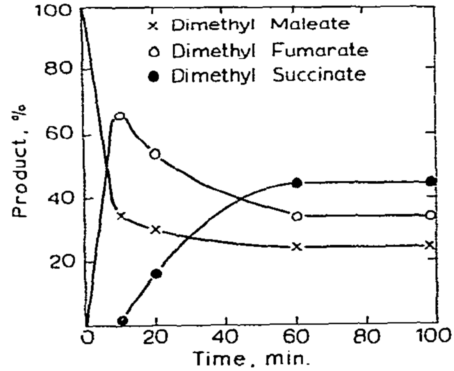


Fig. 1. Dimethyl maleate and $HCo(CO)_4$ (1/1). Dimethyl maleate, 2.25 mmoles; $HCo(CO)_4$, 2.27 mmoles; toluene solvent is 15 ml; temp. 26°; CO atm.; quenched with tripenylphosphine to remove cobalt complexes before analysis.

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* Perkin–Elmer–Hitachi R-MU-6 Mass Spectrometer.

period before the appearance of succinate during which time appreciable fumarate is being formed. Obviously the *trans* isomer hydrogenates more rapidly than the *cis* despite the fact that *cis* olefins coordinate more readily to metals than do the *trans*. In hydrogenation reactions with solid catalysts such as nickel[9] and palladium[10] maleic acid reacts more rapidly than the *trans* isomer. With a soluble ruthenium catalyst, it has been reported[11], without mechanistic elaboration, that fumaric acid hydrogenates more rapidly than maleic acid.

The hydrogenation of pure dimethyl fumarate, Fig. 2, shows that its conversion to succinate is rapid and complete. Theoretically we should expect a stoichiometric ratio of 2 $HCo(CO)_4$/1 olefin and hence a 50% yield. It is interesting that we obtain about a 60% yield and this aspect of the reaction is under investigation.

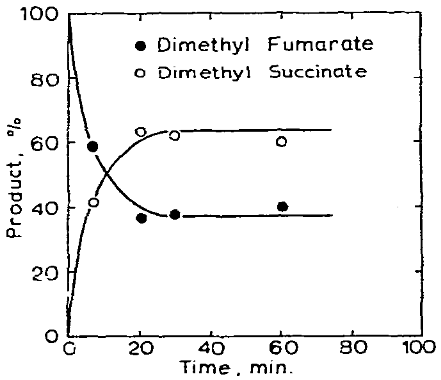
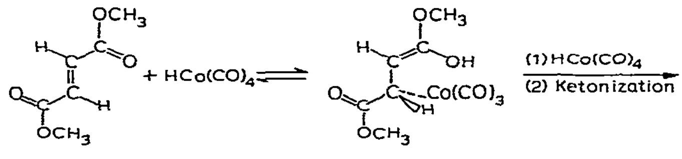


Fig. 2. Dimethyl fumarate and $HCo(CO)_4$ (1/1). Dimethyl fumarate, 2.26 mmoles; $HCo(CO)_4$, 2.27 mmoles; toluene solvent 15 ml; temp. 26°; CO atm.; quenched with triphenylphosphine to remove cobalt complexes before analysis.

The mechanism of the reduction of fumarate and maleate to succinate is of considerable interest. We believe that the addition of hydride to fumarate proceeds principally by a 1,4-addition in contrast to the predominant 1,2-addition to maleate. Usually 1,4-additions proceed through the *s-cis* conformation and the fumarate may present a particularly attractive all *s-cis* conformation:



The intermediate may involve cobalt bonded to carbon either through a *sigma* bond, as shown, or through a π-allyl system. In either case, the intermediate is cleaved by an additional mole of metal hydride and the product ketonizes to the succinate. A comparable *s-cis* conformation of the maleate presents a considerable steric barrier to 1,4-addition.

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