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THE COBALT HYDROCARBONYL-CATALYZED ISOMERIZATION OF ALLYLBENZENE

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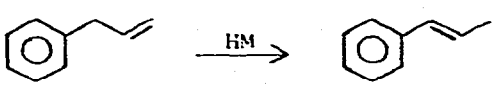
Summary: The $HCo(CO)_4$-catalyzed isomerization of $PhCD_2CH{=}CH_2$ carried out in the presence of an excess of p-allyltoluene gave principally trans-$PhCD{=}CHCH_3$. This result rules out a catalyzed [1,3] sigmatropic shift but is consistent with a 1,2-addition-elimination mechanism.

Introduction: Allylbenzene is rapidly isomerized to trans-propenylbenzene by $HCo(CO)_4$, (HM), at room temperature[1]:



When DM is used in lieu of HM, the rate of isomerization is unchanged and the product contains only about 5 percent D. We originally suggested[1] that this rearrangement might be an example of a 1,3-intramolecular hydrogen shift. This postulate was expanded by an orbital analysis[2] which detailed the manner in which a catalyst might function to promote what could be the first known example of a suprafacial disrotatory [1,3] sigmatropic shift in the allyl system, a process which is normally forbidden on symmetry grounds. However an alternate explanation for the results was advanced[3] which

suggested that the isomerization proceeded by 1,2-Markovnikov addition of DM followed by elimination of HM and continuous cycling of the HM. The purpose of the present investigation was to deduce experimental evidence which might provide the basis for a decision between these alternative mechanisms.

Results and Discussion: A catalytic cycle incorporating the 1,2-addition-elimination mechanism for the isomerization of allylbenzene with $DCo(CO)_4$, (DM), is shown in Fig 1. The first molecule of olefin which isomerizes leads to the π-complex with HM shown in the center of the figure. Now if the second and succeeding molecules of allylbenzene react

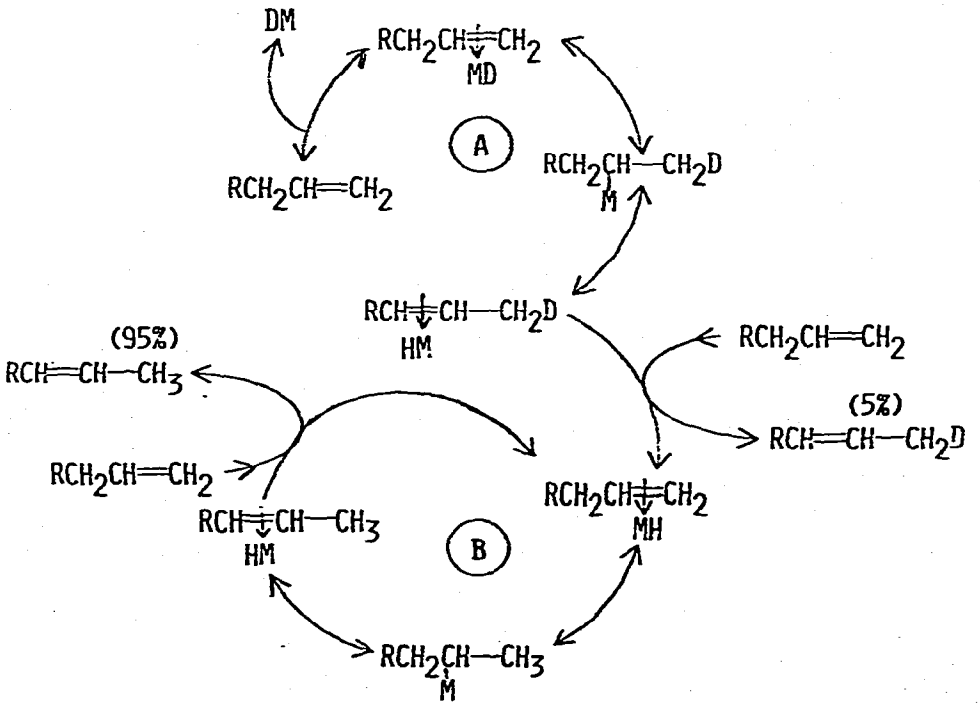


Fig 1. 1,2-Addition-Elimination of DM to $RCH_2-CH=CH_2$ (R = Phenyl).

with coordinated HM rather than with DM, the product of the isomerization should consist of essentially pure unlabelled propenylbenzene. In order to account for the observed result, one need only postulate[3] that this cycle occurs approximately 19 times before allylbenzene again reacts with a molecule of DM; the product, as observed, would thus consist of 95% d_0-propenylbenzene. Were the reaction proceeding exclusively by a [1,3] sigmatropic shift, the product would consist of 100% d_0-propenylbenzene. These numbers are too close to one another to make a rigorous distinction between the processes leading to them.

The use of allylbenzene-α,α-d_2, $PhCD_2CH{=}CH_2$[4], in the presence of an excess of a second olefin which rearranges at about the same rate in the presence of $HCo(CO)_4$, provides a basis for deciding between the alternative mechanisms. The olefin meeting this criterion is p-allyltoluene. The presence, in excess, of this competing olefin serves as a pool for HM and a sink for DM. The competing catalytic cycles are shown in Fig 2. The parts of this figure labelled A and B are essentially identical to those similarly labelled in Fig 1; they describe the isomerization of $PhCD_2CH{=}CH_2$ in the absence of competing allyltoluene leading to $PhCD{=}CHCH_2D$ and thus no substantial loss of deuterium. However, if the π-complex of this compound with MD transfers MD to allyltoluene, part C of Fig 2, then the MD enters cycle D. Following cycle D counterclockwise shows the capture of D and the generation of MH, which in cycle D leads to $PhCD{=}CHCH_3$, and thus loss of deuterium.

In our experiments allylbenzene containing 95% α,α-d_2 was employed and the ratio of it to allyltoluene was 1:4.63 in the isomerization experiments. If one makes the simple

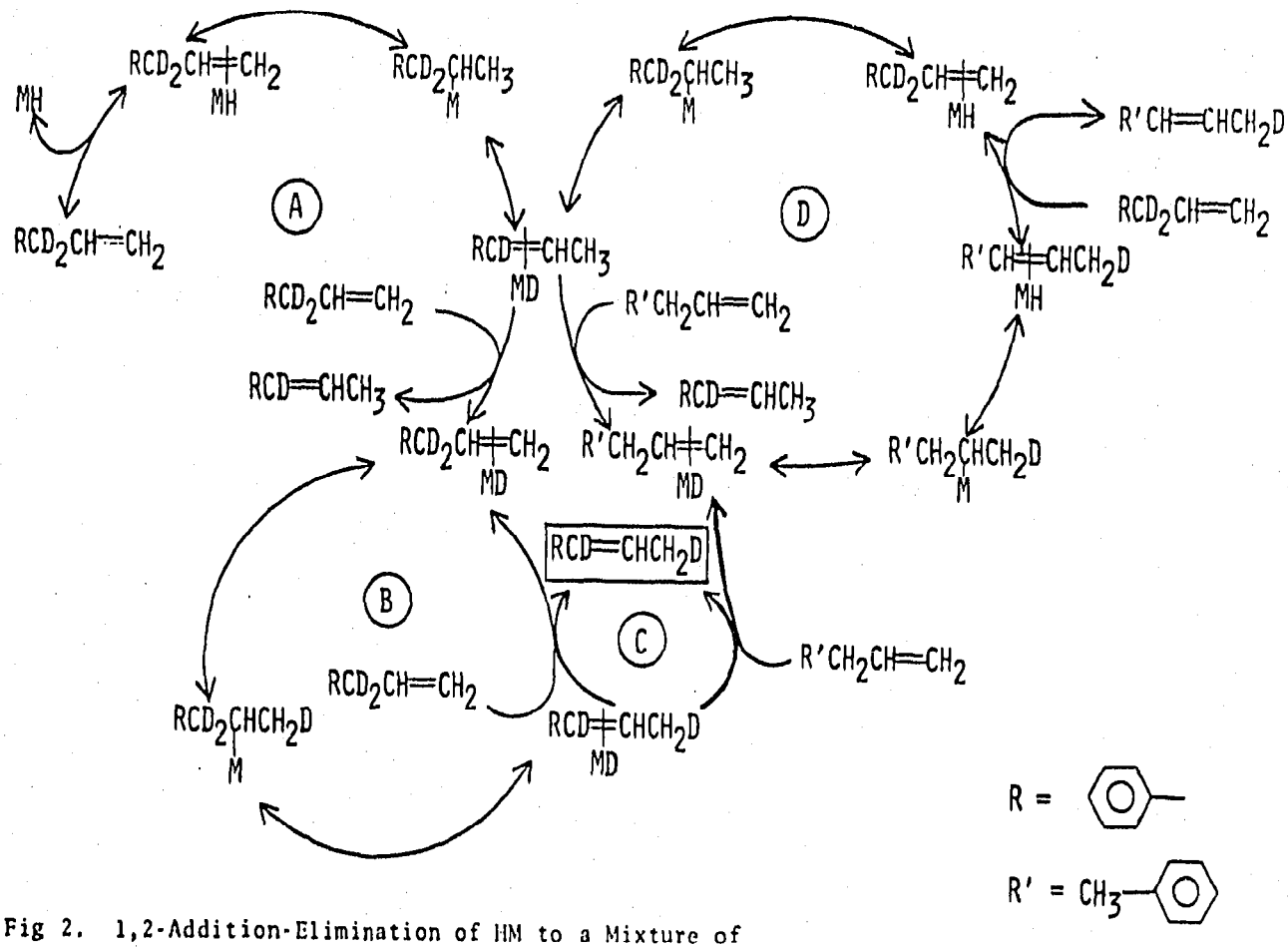


Fig 2. 1,2-Addition-Elimination of HM to a Mixture of $RCD_2CH{=}CH_2$ and $R'CH_2CH{=}CH_2$ (R = Phenyl, R' = p-Tolyl).

assumption that each isomerization of $PhCD_2CH{=}CH_2$ leads to d_2-propenylbenzene and each interception of MD by $R'CH_2CH{=}CH_2$ leads to d_1-propenylbenzene then the ratio of d_2/d_1 should be 1:4.63 or 17.8% d_2, which corrected for 95% purity of the original, is about 17%. Mass spectral analysis of the propenylbenzene showed 15% d_2. The PMR results showed D in all three positions of the side chain. If one assumes that 1,2-addition to the allyl group occurs 70% Markovnikov[4,5], the methyl group of trans-propenylbenzene should contain 2.85 protons and the β-vinyl position should contain 0.94 protons. The results, Table I, show that the 1,2-addition-elimination

TABLE I

ISOTOPE DISTRIBUTION IN TRANS-PROPENYLBENZENE

FROM { 1.00 $PhCD_2CH{=}CH_2$; 4.63 $ArCH_2{-}CH{=}CH_2$ } + $HCo(CO)_4$ $\longrightarrow$ $PhCD{=}CH(D){-}CH_3(D)$

	Calculated, %		
No. of d[a]	Add.-Elim.	[1,3] Sigmat.	Found, %
d_1	78[b]	2	81
d_2	17	95	15
No. of H[c]			
in CH_3	2.85	2.02	2.76
in β-vinyl	.94	1.00	.95

[a]By mass spectra. [b]Neglecting the small amount of d_1 in the original. [c]By ^1H nmr.

mechanism is consistent with experiment and that the [1,3] sigmatropic shift is clearly ruled out.

An important conclusion which emerges from these experiments is the striking preference of the allylaromatics for complexed hydrocarbonyl rather than for free carbonyl. This high preference appears to be related to the presence of the aromatic ring[6].

Experimental: PMR spectra were taken with Varian A-60 and T-60 spectrometers; infrared spectra with a Perkin-Elmer 337 spectrophometer; and mass spectra with a Hitachi-Perkin-Elmer RMU-7 mass spectrometer. A Hewlett-Packard model 700 research gas chromograph was used for product analysis and a Varian 90-P gas chromatograph was used for preparative separations. Solvents were dried by standard methods and all reagents were distilled before use.

Benzyl Alcohol-α,α-d_2. The procedure in the literature[7] was used to prepare the deuterated benzyl alcohol. From 29.43 g of methyl benzoate there was obtained 22.37 g (94%) of benzyl alcohol-α,α-d_2, b.p. 69.3-70.0° (4 mm). The IR, PMR, and mass spectra were all consistent with the assigned structure.

Benzyl Chloride-α,α-d_2. 22.13 g of the benzyl alcohol was converted[7] to 23.26 g (89.9%) benzyl chloride-α,α-d_2, b.p. 59-60.5° (8 mm). The IR, PMR, and mass spectra were consistent with the assigned structure.

Benzylmagnesium Chloride-α,α-d_2. The Grignard reagent was prepared by adding 23.0 g of benzyl chloride-α,α-d_2 in 20 ml of dry ether dropwise to 8.7 g of Mg turnings in 120 ml of dry ether. The rate of addition of the halide was adjusted to maintain gentle refluxing for the 1.5 hr addition period.

The mixture was then stirred for an additional 1.5 hr. 118 ml of Grignard solution was syringed away from the excess magnesium. Titration in the usual manner showed the solution to be 1.46 M, (95.7% yield).

Allylbenzene-α,α-d_2. The Grignard reagent was coupled to vinyl bromide by a modification of the literature procedure[8]. The synthesis was carried out in a series of small scale reactions. Typically an ether solution containing 30 mmoles of Grignard, 114 mmoles of vinyl bromide, and 20.2 g of $NiCl_2(PPh_3)_2$ (31 mmoles) was employed. The Grignard reagent was slowly syringed into a 200 ml pressure bottle flushed with N_2 and containing the vinyl bromide and the Ni complex in ether at -5 to -10°C. The pressure bottle was capped and allowed to come to room temperature. The reaction mixture was stirred at room temperature for approximately 24 hr, then quenched with 50 ml of 2.5 N HCl. The ether phase was separated, washed with $NaHCO_3$, and dried. Distillation at reduced pressure yielded 10.0 g (52%) of allylbenzene-α,α-d_2, b.p. 89-91.5° (100 mm). The IR and PMR spectra were consistent with the assigned structure. The mass spectra results (corrected for ^{13}C) are shown in Table II.

TABLE II

Mass Spectral Data

m/e	Starting Allylbenzene-α,α-d_2 %	Product Trans-Propenylbenzene %
118 (d_0)	--	1.6
119 (d_1)	4.2	81
120 (d_2)	95	16
121 (d_3)	1.0	1.4

Isomerization Experiments. $HCo(CO)_4$ in hexane was prepared by the dimethylformamide (DMF) disproportionation[9] of $Co_2(CO)_8$ followed by acidification at 0° with conc. HCl. The excess HCl was removed by syringe and the $HCo(CO)_4$ solution washed with three portions of CO-saturated H_2O. After as much H_2O as possible was removed, the $HCo(CO)_4$ solution was dried by freezing the remaining H_2O out of solution at acetone/dry ice bath temperature; the $HCo(CO)_4$ solution was then transferred to a CO-flushed flask. The solution was allowed to come to room temperature under CO, then equilibrated in a constant temperature bath at 25.0 ± .1° for 5-10 minutes; its concentration was determined at room temperature by reaction with an excess of NaOH followed by back titration to a phenolphthalein end point.

The $HCo(CO)_4$ solution of known concentration was syringed into a N_2-flushed reaction flask at 25.0 ± .1° which contained hexane sufficient to dilute the $HCo(CO)_4$ so that the desired initial concentration, 0.17 M, was attained on the addition of the olefins. A mixture of 1:1 allylbenzene and allyltoluene was syringed into the reaction flask. Samples were taken at 1 min intervals and quenched with 1.0 M PPh_3 in ethyl ether. The reaction of PPh_3 with $HCo(CO)_4$ is very fast[10] and the product, $HCo(CO)_3PPh_3$, is not a catalyst under these conditions.[11] The solutions were analyzed by VPC on a 15' x 1/4" copper column packed with 20% Carbowax 20M on 60/80 Chromosorb W at an He flow rate of 60 cc/min. The temperature was programmed on injection from 80-120° at 10°/min and held at 120° until the last compound was eluted. The isomerization rate curves were the same shape as those reported previously.[1] The time required for 50% conversion of allylbenzene was 1.1 times that of 4-allyltoluene.

The same isomerization procedure was used as above except that the ratio of allybenzene-α,α-d_2 to 4-allyltoluene was 1:4.63. The reaction was allowed to proceed for 8 min, then 20 ml DMF was added to the reaction mixture and it was stirred until the hexane layer was colorless. The DMF layer was separated and 100 ml of a saturated salt solution was added and this solution was extracted with 25 ml of pentane. The hydrocarbon phases were combined and dried over anhydrous $MgSO_4$, then passed through a column of florisil to remove traces of cobalt complexes. A small quantity of reaction mixture was analyzed by VPC; the results are listed in Table III. The hydrocarbon solvents were removed by

TABLE III

Compounds Identified by VPC[a] (In Order of Elution)

Compound	Mole %
n-Propylbenzene	.7
Allylbenzene	.1
4-n-Propyltoluene	2.8
cis-Propenylbenzene	.7
4-Allyltoluene	.2
trans-Propenylbenzene	15.1
cis-4-Propenyltoluene	3.2
trans-4-Propenyltoluene	77.1

[a]From the reaction between a mixture of allylbenzene-α,α-d_2 and 4-allyltoluene (1:4.63 ratio) with $HCo(CO)_4$ (3:1 olefin to cobalt ratio) under nitrogen at 25°C for 8 minutes.

distillation, and the trans-propenylbenzene was isolated by preparative VPC; its mass and PMR spectra were determined. The authentic trans-propenylbenzene and the isolated product gave the following mass spectra at 5 ev: m/e (relative intensity): Authentic sample; 118 (100.0), 119 (11.7), 120 (1.5). Isolated sample; 118 (2.0), 119 (100.0), 120 (31.4), 121 (5.5). The isotope distribution was calculated on the basis of these data, after correcting for normally occurring isotopes (C^{13}). The PMR spectrum of the isolated trans-propenylbenzene gave ($CDCl_3$) δ 7.28 (S, 5H), 6.22 (twelve-line multiplet, 0.95H, J = 2.3 Hz), 1.82 (D, 2.76 H, J = 6.5 Hz).

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