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The Mechanism of the Rearrangement of the Hydrocobalt Carbonyl Catalyzed Isomerization of 3-Phenylpropene

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Abstract: The *trans*-1-phenylpropene produced in the $HCo(CO)_4$ catalyzed rearrangement of 3-phenylpropene-3,3-d_2 was found, by NMR analysis, to contain appreciable deuterium in the 2 position as well as the 1 and 3 positions of the propenyl system. No protium was observed in the 1 position. These results are consistent with the 1,2 addition–elimination mechanism which has previously been postulated to occur in other cobalt carbonyl induced isomerizations of alkenes containing no aryl substituents and are not compatible with the suggestion that intramolecular 1,3-hydrogen shifts are predominant in "activated" systems containing an aryl group.

The isomerization of olefins catalyzed by transition metal complexes has been an important and extensively studied aspect of organometallic chemistry.[1] As has been recently pointed out,[1] there are now two commonly accepted mechanisms, depending on the catalyst system, for such isomerizations. One involves an intramolecular 1,3-hydrogen shift and the other a 1,2 addition–elimination mechanism.

It now seems to be no question but that the isomerization of allylic alcohols with either iron pentacarbonyl or triiron dodecacarbonyl involves an intramolecular 1,3-hydrogen shift.[2] Whether the mechanism proceeds via a π-allyl metal hydride intermediate as initially proposed by Pettit and Emerson,[3] or a concerted mechanism[2b] involving some iron–hydrogen bonding in the transition state, has not been unequivocally established. Recently, Casey and Cyr demonstrated that the triiron dodecacarbonyl-induced rearrangement of 3-ethyl-1-pentene occurred via an intramolecular 1,3-hydrogen shift in which the rate of isomerization of complexed alkene was rapid in comparison with the rate of decomplexation.[1] A π-allyl metal hydride intermediate was postulated to account for the isomerization. In support of this mechanism is the recent report of the first direct observation of a π-allyl–hydride exchange in a π-allyl–molybdenum hydride complex.[4]

The mode of hydrogen transfer in olefin isomerizations with cobalt carbonyls is not so clearly established. Thus it has been shown that olefin isomerizations accompanying the hydroformylation of 3-methyl-1-hexene-3-*d*, initiated by dicobalt octacarbonyl, proceeds by way of a metal hydride addition–elimination mechanism.[5] Similarily, Taylor and Orchin concluded that the $HCo(CO)_4$ catalyzed rearrangement of propene-d_6 proceeded at least in part by the 1,2 addition–elimination of $HCo(CO)_4$.[6] However, in the $DCo(CO)_4$ catalyzed rearrangement of allyl alcohol to propionaldehyde, evidence was obtained for a 1,3 intramolecular hydrogen shift.[7] Also during the isomerization of allylbenzene catalyzed by $DCo(CO)_4$, it was found that the product, β-methylstyrene, contained only about 5% deuterium.[8] These results were stated as not being compatible with an addition–elimination mechanism, and an internal 1,3-hydrogen shift was proposed to account for most of the reaction.[8] To explain the apparent duality of mechanisms, Hubert and Reimlinger have suggested that both types of hydrogen transfer can take place separately or simultaneously.[9] Thus it was proposed that the addition–elimination mechanism would predominate with simple olefins but that with olefins containing an activated allylic hydrogen, e.g., allylbenzene, such hydrogens would be more mobile than the hydrogen bonded to the metal and a 1,3 intramolecular hydrogen transfer would be the preferred mode of isomerization. However, Cramer and Lindsey have questioned the necessity of postulating an internal 1,3-hydrogen shift to explain the small amount of deuterium incorporation accompanying the $DCo(CO)_4$ catalyzed isomerization of allylbenzene and have suggested that the data are completely explicable in terms of an addition–elimination mechanism.[10] While others[5] have concurred with Cramer and Lindsey's interpretation of Orchin's data, experimental verification of this interpretation has not yet been provided.

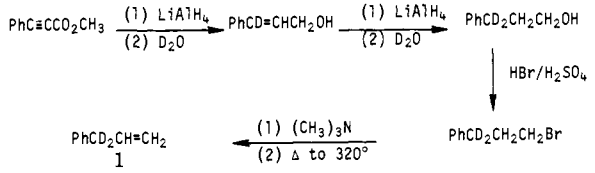
In an effort to clarify these ambiguities, we have prepared 3-phenylpropene-3,3-d_2 and have studied its rearrangement with $HCo(CO)_4$.

Results

Synthesis. It was necessary to prepare 3-phenylpropene-3,3-d_2 (**1**) with a high degree of isotopic purity and in relatively

large quantities. The general procedure employed, outlined in Scheme I, resulted from an extension of work already in the literature.[11]

Scheme I



Final distillation through a spinning-band column gave >99% pure (VPC) **1** for which no signal for benzylic proton (less than 1%) was observed in the NMR spectrum.

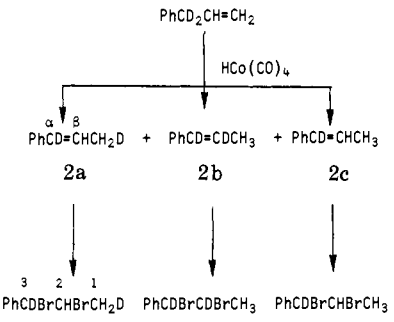
Rearrangement of 1 with $HCo(CO)_4$. The procedure used by Roos and Orchin was followed as closely as details permitted.[8] Thus rearrangement was accomplished by warming a mixture of $HCo(CO)_4$, hexane, and **1** to 35 °C for about 3 min. The product mixture (see Scheme II) was analyzed by VPC and was found to consist of *n*-propylbenzene (14%), allylbenzene (1%), *cis*-1-phenylpropene (5%), and *trans*-1-phenylpropene (**2**) (80%). The NMR spectrum of **2** showed a broad singlet at δ 7.12 due to the phenyl protons which was assigned a relative integrated area of five protons, a broad multiplet containing at least twelve unresolved peaks at δ 6.01 (β-vinyl), and a broad multiplet at δ 1.67 (methyl). The phenyl:β-vinyl:methyl proton ratio was 5.00:0.71:2.33, respectively. There was *no* signal at δ 6.28 which indicated the absence (less than 1%) of any protons on the α-vinyl carbon. Upon decoupling of the deuterium, the signal at δ 6.01 was resolved into a seven-line multiplet consisting of what appeared to be a quartet (J = 6.6 Hz) superimposed on a triplet (J = 6.6 Hz). The signal at δ 1.67 was resolved into a sharp "triplet" consisting of a singlet superimposed on a doublet (J = 6.6 Hz).

Compound **2** was brominated, and the spectrum of the deuterated *erythro*-1,2-dibromo-1-phenylpropane showed a broad singlet at δ 7.23 (phenyl), a broad multiplet at δ 4.46 (C_2), and a broad multiplet at δ 1.95 (C_3). The phenyl:C_2:C_3 proton ratio (relative to phenyl equal to five protons) was 5.00:0.67 ± 0.03:2.28 ± 0.06, respectively, averaged over 40 integrations. There was *no* signal at δ 4.97 (C_1). The deuterium magnetic resonance spectrum of the dibromo derivative showed three broad singlets at δ 5.0 (C_1), 4.5 (C_2), and 2.0 (C_3) in a ratio of 1.00:0.35:0.62, respectively. No deuterium resonance at δ 7.23 (phenyl) was seen.

Discussion

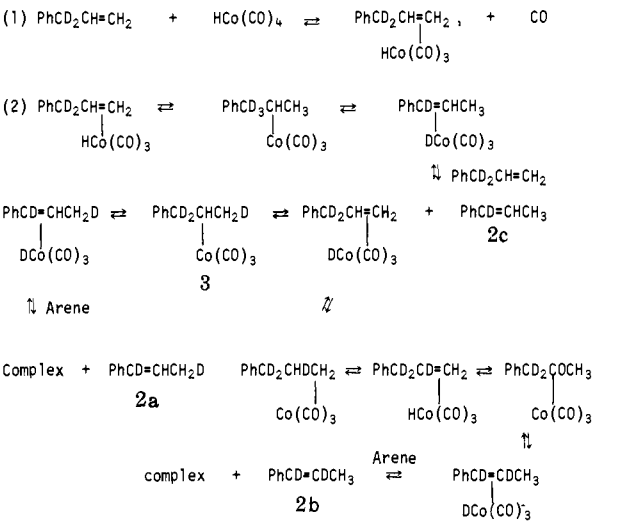
To be consistent with the evidence above, no product may have a proton in the α-vinyl position, and approximately 35% of the product should have deuterium in the β-vinyl position. Products **2a** and **2b** shown in Scheme II are consistent with

Scheme II



these restrictions. However, if these were the only two products, the β-vinyl proton in **2** (δ 6.01) would be predicted to be a triplet. As was mentioned previously, upon decoupling of deuterium, the signal was resolved into a seven-line multiplet which appeared to be due to a quartet superimposed on a triplet. It is therefore suggested that a small but observable amount of **2c** was formed as would be expected in accordance with the mechanism proposed in Scheme III. The formation

Scheme III



of additional products, which however were not detected, can also be rationalized by this scheme.

If step 1 in Scheme III is slow in comparison to ligand rearrangement in the various complexes and with respect to ligand exchange, only small amounts of **2c** would be formed. This indeed was observed and is in accord with the interpretation[10] postulated to explain the small amount of the deuterium incorporation in the $DCo(CO)_4$ catalyzed rearrangement of allylbenzene performed by Orchin.[8] The two major products which were formed, **2a** and **2b**, would occur by the facile olefin rearrangement and ligand exchange processes.

It is interesting to note that **2a** accounts for approximately 65% of the product and results from addition of the metal atom to the secondary carbon in formation of **3**. This is in excellent accord with Orchin's results where he obtained 70% of such Markovnikov addition in the isomerization of propene with $HCo(CO)_4$.[6]

Out data are thus *completely* explicable in terms of the 1,2 addition–elimination mechanism which has been found to be operative in other cobalt carbonyl catalyzed isomerizations.[5,6] Furthermore, since all of the available experimental evidence can be *completely* explained by the 1,2 shift mechanism there is no need of postulating a concurrent mechanism involving an intramolecular 1,3-hydrogen shift, which could *at best* rationalize only about 65% of the experimental data.[12] Indeed, if such a process were operative, one would have expected to find, contrary to our results, some proton in the α-vinyl position, for it has been demonstrated that 1,3-hydrogen transfers are reversible in other systems.[1,4] It should be noted also that rearrangement of **1** with $Fe(CO)_5$ resulted in essentially complete equilibrium exchange of deuterium between the α-vinyl and methyl positions with no deuterium detected in the β-vinyl position.[13]

Experimental Section

NMR spectra were recorded on a Varian A-60 or Brucker HX90 spectrometer using Me_4Si as an internal standard. Analytical GLC were performed on a Varian Model 600D and a F & M 810, while for preparative GLC a Varian A-700 was used. A 9 ft × ⅛ in. 10% Carbowax (A), 10 ft 10% Carbowax (B), and a 3 m 20% Carbowax (C) on Chromosorb G-AW were employed in the 600-D, F & M, and A-700 instruments, respectively. Melting points were obtained on a Thomas Hoover capillary apparatus and are uncorrected.

3-Phenylpropenol-3-*d*. By an adaptation of the method of Bates, Jones, and Whiting,[11b] 9.0 g of methyl phenylpropiolate dissolved in

40 ml of anhydrous ether was added slowly to a stirred mixture of 2.16 g of $LiAlH_4$ in 150 ml of anhydrous ether. After refluxing for 15 min the reaction mixture was cooled in an ice bath and 2 ml of D_2O was added slowly. To ensure complete reaction, 1 ml of 20% DCl in D_2O was added, and the reaction mixture was then refluxed for 10 min, cooled, and subjected to hydrolysis by the addition of 70 ml of 20% H_2SO_4. The aqueous layer was extracted with ether and worked up in the usual manner. Distillation gave 6.82 g (89%) of 3-phenylpropenol-3-*d*, bp 80 °C (0.3 mm) which solidified upon cooling: mp 33 °C; ^1H NMR (neat) δ 7.17 (S, 5 H), 6.2 (t, 2 H, J = 5.8 Hz), 4.2 (d, 2 H, J = 5.8 Hz), 4.9 (S, 1 H). No signal was observed at δ 6.55 (α-vinyl).

3-Phenylpropanol-3,3-d_2. According to the general procedure of Hochstein and Brown,[11a] 87 g of 3-phenylpropenol-3-*d* dissolved in 200 ml of anhydrous ether was added slowly to 13 g of $LiAlH_4$ in 150 ml of ether. After refluxing for 3 h, the reaction mixture was cooled in an ice bath, and 17 ml of D_2O was added slowly. Next was added 5 ml of 20% DCl in D_2O, and the reaction mixture was refluxed for 1.5 h. The cooled solution was hydrolyzed by the addition of 700 ml of 20% ether, and worked up in the usual manner. Distillation gave 82 g of 3-phenylpropanol-3,3-d_2: bp 132 °C (21 mm); ^1H NMR ($CDCl_3$) δ 2.83 (S), 8.3 (t, J = 6.8 Hz), 6.5 (t, J = 6.8 Hz), 6.0 (S). No signal was observed at δ 7.14 (benzylic).

1-Bromo-3-phenylpropane-3,3-d_2. To 82 g of 3-phenylpropanol-3,3-d_2 was added 280 ml of 48% HBr with stirring, and the solution was refluxed for 1 h. The solution was then cooled and 45 ml of concentrated H_2SO_4 added. After additional refluxing for 30 min, 20 ml of H_2SO_4 was again added to the cooled solution. The water-insoluble layer was washed with water and 10% Na_2CO_3 until neutral. Distillation gave 94.4 g (77%) of 1-bromo-3-phenylpropane-3,3-d_2, bp 58 °C (0.05 mm): ^1H NMR (neat) δ 7.1 (S), 1.9 (t, J = 6.8 Hz), 3.1 (t, J = 6.8 Hz). There was no signal at δ 7.5 (benzylic).

Trimethylhydrocinnamylammonium-d_2 Bromide. Following the procedure of Hochstein and Brown,[11a] to a mechanically stirred solution of 40.2 g of 1-bromo-3-phenylpropane-3,3-d_2 was added 270 ml of a solution containing 65 ml of trimethylamine in 400 ml of anhydrous ethanol. The reaction flask was equipped with a reflux condenser using recirculated salt water (−10 °C) and topped with a dry ice/acetone filled cold finger. After refluxing for 3 h, the mixture was cooled in an ice–salt bath, trimethylamine was added, and the mixture was refluxed for an additional 3 h. The crude solid obtained by addition of pentane was recrystallized from ethanol/pentane to yield 48.6 g (97%) of the quaternary bromide, mp 149–150 °C.

3-Phenylpropene-3,3-d_2 (1). Pyrolysis of 26 g of trimethylhydrocinnamylammonium-d_2 bromide at 320 °C in the manner of Hochstein and Brown[11a] yielded 8.3 g (71%) of 3-phenylpropene-3,3-d_2 upon distillation. Further distillation via a spinning-band column (bp 156–157 °C) gave >99% 3-phenylpropene (GLC): ^1H NMR (neat) δ 6.87 (S, 5 H), 5.68 (m, 1 H), 4.91 (m, 1 H), 4.69 (m, 1 H). There was no signal at δ 3.10 (benzylic).

Rearrangement of 3-Phenylpropene-3,3-d_2 (1) with $HCo(CO)_4$. The procedure used by Roos and Orchin[8] was followed as closely as details permitted. Thus 40 ml of a dry hexane solution of $HCo(CO_4)$ (7.2 mmol) was injected via a rubber septum into a flask containing 2.40 ml (21.6 mmol) of **1** at −80 °C under a N_2 atmosphere. The frozen mixture was warmed to 35 °C and allowed to react for 3 min. After cooling slowly to 0 °C (in 3 min), the solution was poured into 100 ml of 3% NaOH solution. The organic portion was separated in the usual manner and distilled to yield 1.81 g of crude product, bp 30 °C (2.0 mm). Analysis by GLC (column A, 200 °C) showed the product to consist of *n*-propylbenzene (14%), allylbenzene (1%), *cis*-1-phenylpropene (5%), and *trans*-1-phenylpropene (**2**) (80%). The latter was purified by preparative GLC (column C); ^1H NMR (neat) δ 7.12 (broad s, 5 H), 6.01 (seven-line multiplet, 0.71 H, J = 6.6 Hz), 1.67 ("triplet", 2.33 H, J = 6.6 Hz). There was no signal at δ 6.28 (α-vinyl).

***erythro*-1,2-Dibromo-1-phenylpropane.** A 10% solution of **2** in CCl_4 was cooled to 0 °C, and 10% Br_2 (CCl_4) was added until the red color persisted. The solution, after stirring for 15 h, yielded pure erythro dibromide: mp 66–67 °C (lit. 66–67 °C);[14] ^1H NMR (CCl_4) δ 7.23 (S, 5 H), 4.46 (seven-line multiplet, 0.67 H), 1.95 ("triplet", 2.30 H). There was no signal at δ 4.97: ^2H NMR (CCl_4), δ 5.0 (1.00 D), 4.5 (0.35 D), 2.0 (0.62 D). No signal was observed at δ 7.2.

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(12) A referee has raised the objection that the real question is whether the reaction is partially intramolecular even though the metal hydride addition–elimination mechanism can explain all the results. However, since a 1,3 intramolecular hydrogen transfer does not explain any additional available information, we believe its inclusion at this time to be unwarranted.
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