Catalysis of the Cope Rearrangement by Alumina

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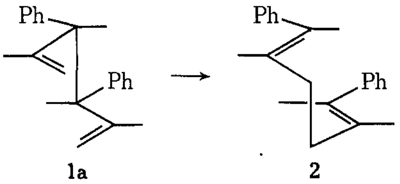
During attempted chromatographic purification of *dl*-3,4-diphenylhexa-1,5-diene (**1**) on alumina (Woelm 200, neutral, grade super I), the unexpected and surprising observation was made[1] that the diene had been partly converted to *trans,trans*-1,6-diphenylhexa-1,5-diene (**2**), the product of its thermal Cope rearrangement at 80 °C via a chairlike transition state (**1a**).[2] We report here a more detailed investigation of this phenomenon, including examination of the corresponding meso diene (**3**) which likewise rearranges on alumina, although at a considerably slower rate, to a product mixture comparable to that of its purely thermal Cope rearrangement, namely, *cis,trans*- (**4**) and *trans,trans*-1,6-diphenylhexa-1,5-diene (**5**).[2] To achieve convenient rearrangement rates, the commercial alumina was further activated for 4 h at 650–700 °C, a temperature which is reported to yield a catalyst of maximum activity.[3]



1a **2**

With an alumina:diene ratio of 50:1, approximately 20 mg of *dl* diene (**1**) in 1 ml of heptane was converted within 15 min at room temperature to the trans,trans diene (**2**). The infrared spectrum of the crude product (84% material recovery) was virtually identical with that of authentic material, and VPC analysis showed less than 0.1% of other products under conditions where the three isomeric 1,6-diphenylhexa-1,5-dienes as well as *trans*-1,4-diphenylhexa-1,5-diene are resolved. Using Woelm 200 neutral alumina directly from its container without further activation, essentially equivalent results were obtained in 70 h at room temperature, as well as in 1.5 h at 60 °C. The uncatalyzed Cope rearrangement of the *dl* diene has a half-life of about 8 h at 80 °C and yields exclusively the trans,trans diene.[2]

Investigation of the meso diene rearrangement was complicated by incomplete conversions as well as alumina-catalyzed product isomerization. The extent of conversion could be determined by quantitative infrared spectroscopy on the crude rearrangement mixture, and product analysis was again carried out by VPC, after separation of the thermally labile unconverted meso diene by thin layer chromatography on silver nitrate impregnated silica gel.

Table I summarizes the results of two rearrangements at room temperature under conditions similar to those employed for *dl* diene. It is apparent from the leveling off of the percent rearrangement with time, especially in run 2, that the catalyst is becoming deactivated, and some product isomerization may be taking place. The inconsistencies in percent rearrangement with time are characteristic of the difficulties and poor reproducibility encountered in the investigation of the meso diene rearrangement. The sample points represent individual ampules, and the reaction is apparently sensitive to slight variations in the preparation and handling of the highly active catalyst. Accepting the data of run 1 as the more consistent, the alumina-catalyzed rearrangement of meso diene at room temperature gives 68% of *cis,trans*- (**4**) and 32% of *trans,trans*-1,6-diphenylhexa-1,5-diene (**5**).

Table I. Meso Diene Rearrangement at Room Temperature

Run 1

Reaction time, min	15	30	45	60
% meso diene rearranged	11	15	20	21
% cis,trans	68	68	68	68
% trans,trans	32	32	32	32
% material recovery	85	94	85	85

Run 2

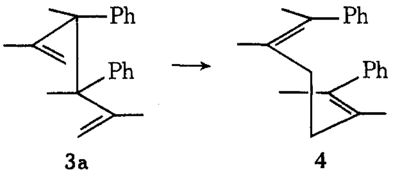
Reaction time, h	1	2	3	4
% meso diene rearranged	36	33	40	37
% cis,trans	73	72	68	69
% trans,trans	27	28	32	31
% material recovery	78	79	90	87

Table II. Meso Diene Rearrangement at 60 °C

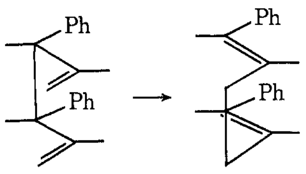
Reaction time, min	15	30	45	60
% meso diene rearranged	53	96	82	"110"
% cis,trans	46	34	23	23
% trans,trans	54	66	77	77
% material recovery	95	75	90	73

Results of catalyzed rearrangement at 60 °C are given in Table II. Product isomerization is pronounced, and a rough approximation of the isomer ratio formed in the rearrangement itself, obtained by extrapolation to zero time, is 55% of cis,trans and 45% trans,trans isomers. Inconsistencies are again apparent in the extent of rearrangement vs. time.

The alumina-catalyzed rearrangement of the meso diene is likewise seen to parallel its purely thermal Cope rearrangement. In this case both the chairlike (**3a**) and boatlike (**3b**) configurations are involved, leading respectively to the cis,trans and trans,trans products. The thermal rearrangement gives 63% cis,trans and 37% trans,trans diene at 120 °C with a half-life of about 15 h.[2]



3a **4**

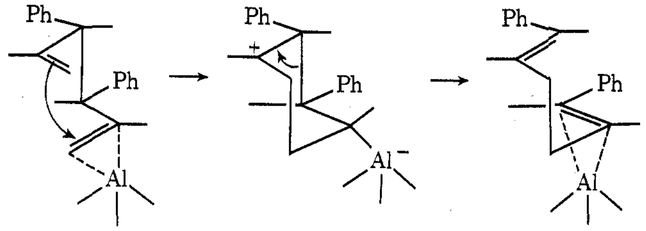


3b **5**

To rule out the possibility that catalyzed rearrangement arises from a fragmentation–recombination process involving phenyl-substituted allyl radicals and *trans*-1,4-diphenylhexa-1,5-diene as intermediates, the latter was subjected to the conditions of catalyzed rearrangement. It was unaffected by this treatment, and was also not detected in any of the crude rearrangement products.

The parallelism between the alumina-catalyzed and thermal reactions suggests that catalysis involves interaction of only one double bond with the catalyst surface, leaving the other free to adopt the preferred configuration. Assuming that catalysis by alumina is a consequence of Lewis acidity, some variation of the process illustrated in Scheme I for the *dl* diene may be operating in the catalyzed reaction.

Scheme I



A few examples of catalyzed Cope rearrangements have been previously reported, each involving a transition metal complex.[4] The oxa-Cope (Claisen) rearrangement is catalyzed by more or less ordinary Lewis acids.[5]

Experimental Section

Melting points are uncorrected and were obtained in capillary tubes. Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. VPC analysis of the systems under study has already been described.[2] TLC analyses were on silica gel (Merck, HF_{254}) impregnated with about 20% silver nitrate, with sample components directly visible under short-wavelength uv light or upon spraying with 2,7-dichlorofluorescein followed by long-wavelength uv. Except where noted, alumina (Woelm 200, neutral, grade super I, approximately 200 m^2/g BET surface area) was activated at 650–700 °C for 4 h prior to use. Weighings of alumina were carried out in a drybox. *n*-Heptane (Mallinckrodt spectrophotometric grade) was dried over molecular sieves.

Rearrangement of *dl*-3,4-Diphenylhexa-1,5-diene on Aluminum Oxide. Approximately 1 g of alumina was weighed into each of four 5-ml Pyrex ampules; into each ampule was injected a solution of *dl* diene (mp 34.7–35.6 °C) in *n*-heptane (20 mg/ml) in such quantity that the diene:alumina ratio was 1:50. The ampules were closed with serum caps and left at room temperature with frequent manual shaking for 15, 30, 45, and 60 min, respectively. Crude products were isolated by vacuum evaporation of solvent after filtration and rinsing of the pale yellow alumina with a small amount of methanol. The ir spectra of all samples were virtually identical with that of authentic *trans,trans*-1,6-diphenylhexa-1,5-diene. VPC confirmed that this was the major component, with only traces of other materials; isomeric 1,6-diphenylhexa-1,5-dienes were absent in amounts greater than 0.1%. Melting points and percent material recovery for the crude samples follow: 15 min (84%), mp 74.0–77.2 °C; 30 min (94%), 73.5–76.7 °C; 45 min (87%), 75.5–77.5 °C; 60 min (84%), 73.5–76.0 °C; lit.[2] 79.0–79.5 °C.

Another run used 20 mg of *dl* diene in 2 ml of *n*-heptane with 2 g of Woelm alumina taken directly from its container without further heating. Rearrangement was monitored by TLC (development in 1:1 carbon tetrachloride–acetone); the reaction appeared complete after 70 h. The crude product, mp 73.5–76.0 °C, analyzed by VPC as *trans,trans*-1,6-diphenylhexa-1,5-diene with only traces of other components.

A similar run was carried out at 60 °C with 40 mg of *dl* diene in 2 ml of *n*-heptane and 2 g of Woelm alumina taken directly from its container. VPC analysis of the crude product (mp 76.0–77.5 °C) after 1.5 h showed no significant components other than the trans,trans diene.

Rearrangement of *meso*-3,4-Diphenylhexa-1,5-diene on Aluminum Oxide. Run 1. Into each of four ampules containing approximately 1 g of alumina was injected a solution of meso diene (mp 85.6–86.5 °C) in *n*-heptane (25 mg/ml) in such quantity that the diene:alumina ratio was 1:50. Crude products were isolated after 15, 30, 45, and 60 min at room temperature. The ir spectrum of each was determined quantitatively, following which unreacted meso diene was removed by preparative TLC (70:30 carbon tetrachloride–acetone). The faster moving unresolved 1,6-diphenylhexa-1,5-dienes were eluted from the silica gel with dichloromethane. VPC analysis identified *cis,trans*- and *trans,trans*-1,6-diphenylhexa-1,5-diene as the only products present in other than trace amount, with their relative ratios determined by integration. The percent conversion for each sample was determined from the intensity of the 10.4-μ ir band common to the two dienes, employing an average extinction coefficient calculated from the VPC data and the extinction coefficients for the pure cis,trans diene (0.67 ml mg^{-1} cm^{-1}) and the trans,trans diene (1.97 ml mg^{-1} cm^{-1}). Results are shown in Table I.

Run 2. In a second run ampules were kept at room temperature for 1, 2, 3, and 4 h, respectively. Results are given in Table I. Characteristics of this run were similar to those of the earlier one, except that the later samples showed a slight unidentified shoulder on the downward slope of the VPC trace of the trans,trans diene.

A third run was carried out at 60 °C, with crude products isolated at 15, 30, 45, and 60 min. Results are given in Table II. A trace component with a retention time corresponding to that of *cis,cis*-1,6-diphenylhexa-1,5-diene could also be observed in the VPC traces. The "110%" conversion in 60 min probably reflects inability to isolate product absorption at 10.4 μ from background ir absorption, since pure trans,trans diene showed linearity in the concentration range employed. Visual inspection of the ir spectrum actually suggested approximately 5% unreacted meso diene after 60 min. No attempt was made to improve the ir analysis in view of the inherent lack of reproducibility encountered and expected in a heterogeneous system involving a highly activated alumina.

Stability of *trans*-1,4-Diphenylhexa-1,5-diene on Alumina. Two ampules prepared as above using *trans*-1,4-diphenylhexa-1,5-diene in *n*-heptane were maintained, respectively, at room temperature for 4 h and at 60 °C for 1 h. Isolation of the diene followed by ir and VPC examination showed that the trans 1,4-diene had undergone no change.

Registry No.—**1**, 33788-15-7; **2**, 58463-02-8; **3**, 33788-14-6; **4**, 33788-20-4; alumina, 1344-28-1.

References and Notes

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Carboxylation of Aromatic Compounds by Palladium(II) Carboxylates

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Benzenoid compounds react with palladium(II) salts in a variety of ways, depending on the reaction conditions used. The products resulting from chlorination,[1] acetoxylation,[2] nitration,[3] carbonylation,[4] and oxidative dimerization[5] are known. The authors have already communicated a newer type of reaction by palladium(II) chloride and sodium acetate, i.e., aromatic carboxylation.[6] However, the yields of aromatic acids therein produced were relatively poor.

The present paper describes that the use of palladium(II) carboxylates improves the yields of aromatic acids and that the olefinic hydrogen of styrene is also substituted by carboxyl group, although in a low yield.

The reaction of aromatic compounds with sodium palladium(II) malonate (A)[7] in a mixed solvent of acetic acids and acetic anhydride or carbon tetrachloride gave aromatic acids in good yields, together with lower yields of aromatic dimers. The results are shown in Table I. It can be seen that sodium palladium(II) malonate (A) is much more efficient for aromatic carboxylation than the palladium(II) chloride–sodium acetate system.[6]