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A Photoassisted Hole-Catalyzed Cope Reaction on Zeolite

The photoassisted, zeolite-catalyzed Cope rearrangement of 1,3,4-triphenyl–1,5-hexadiene is reported and is proposed as the first example of a single electron acceptor (hole)-catalyzed Cope reaction. The [3,3] sigmatropic reaction in which a 1,5-hexadiene rearranges to an isomeric 1,5-hexadiene (the Cope reaction, e.g., **1** → **2** in Scheme 1) is a reaction of substantial synthetic value, and considerable effort has therefore been expended on the development of catalytic forms of the reaction. Typically these forms have exploited the acidity or basicity of a specifically placed heteroatom substituent (e.g., the base-promoted oxy-Cope and Brønsted acid-catalyzed Cope) (*1, 2*). More recently a palladium (II) chloride-catalyzed version of the Cope reaction of several hydrocarbon 1,5-dienes has also been developed (*3*). This, too, appears to have a specific requirement, that of an alkyl substituent at the 2 (and/or 5) position. Most recently, observations of hole (single electron acceptor) catalysis of the Diels–Alder and olefin cycloaddition reactions have led to the suggestion that hole catalysis may represent a powerful catalytic principle for a variety of pericyclic reaction types (*4–9*). Theoretical calculations suggest that the hole-catalyzed Cope reaction should proceed without significant activation energy once the 1,5-diene cation radical has been generated, assuming the rearranged 1,5-diene cation radical is sufficiently stable to render the rearrangement thermodynamically favorable (*9*). Several hole-catalytic systems have been developed for the Diels–Alder reaction, including soluble aminium salts, cation radical polymers, photosensitized electron transfer, and zeolites (the latter with the option of photoassistance) (*4–11*). In this paper, the first instance of a hole-catalyzed Cope reaction is reported, and it is found that, at least for this reaction, zeolites represent by far the most efficient catalyst systems.

METHODS

Racemic erythro- and threo-1,3,4-triphenyl-1,5-hexadiene (**1**) were, respectively, prepared in 86% yield from *erythro*- and *threo*-2,3-diphenyl–4-pentenal (1.0 eq) and benzylidene triphenylphosphorane (1.1 eq; prepared from 1.2 eq of benzyltriphenylphosphonium bromide and 1.1 eq of *n*-butyl lithium at −78°C in THF, followed by warming to 0°C over 2 h) at 0°C in THF. After 24 h at 0°C, the reaction mixture was worked up by adding water and hexane and repeatedly extracting the hexane solution with brine to remove the THF. Evaporation of the hexane, followed by flash column chromatography on silica gel afforded an 86% yield of **1** as a yellow oil. The latter was characterized by ^{1}H and ^{13}C NMR spectroscopy, GCMS, and high-resolution MS. The *erythro* and *threo* diastereoisomers, when thus prepared, were of course racemic and also consisted of a mixture of Z and E (predominantly Z) geometric isomers, which were not further separated. The requisite aldehyde precursor was obtained in 80% yield by refluxing cinnamyl alcohol (0.14 mole) with phenylacetaldehyde dimethylacetal (0.16 mole) in 125 ml of mesitylene containing *o*-nitrobenzoic acid (0.047 mole, as an acid catalyst), and distilling off the methanol under nitrogen (*12*). The aldehyde thus obtained was a 1 : 1 mixture of *erythro* : *threo* diastereoisomers from which the less-soluble *erythro* isomer was readily obtained by crystalli-

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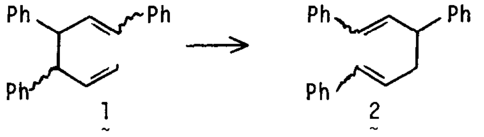


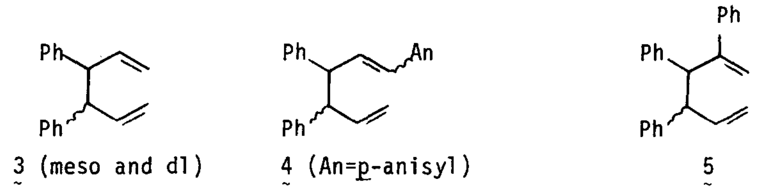
SCHEME 1

zation from hexane (mp 94.5–98°C). The remaining *threo*-enriched aldehyde was subjected to vacuum distillation (bp 115–130°C; 0.5 Torr) and repeated recrystallizations from hexane to yield the nearly pure *threo* isomer. The 13X zeolites were obtained from the Aldrich Company and used directly. The hole-catalyzed Cope rearrangement of **1** was accomplished by dissolving 34.6 mg of **1** in 8 ml of freshly distilled, dry dichloromethane (DCM) in a Pyrex test tube and adding approx. 4.7 g of 13X zeolites. After the tube was stoppered, the reaction was irradiated with a 450-W Hanovia medium-pressure UV lamp for 40.5 h. Simultaneous control reactions in which either the zeolite or UV light was not provided confirmed the co-requirements of catalyst and light. The product was worked up by filtering the zeolites and washing them repeatedly with DCM and then acetonitrile. After evaporation of the combined solvents and chromatography by reverse-phase semipreparative HPLC (90 : 10 acetonitrile : water), a 54% yield of 1,3,6-triphenyl-1,5-hexadiene (**2**) was obtained, also as a mixture of geometric isomers.

RESULTS

The uncatalyzed, thermal Cope rearrangement of *erythro*- and *threo*-1,3,4-triphenyl-1,5-hexadiene (**1**) to 1,3,6-triphenyl-1,5-hexadiene (**2**) proceeds smoothly to completion (135°C, 1.5 h), presumably as a result of the thermodynamic driving force associated with the creation of the additional styrene-type conjugated system in **2**. Attempted hole catalysis of this rearrangement using the stable cation radical salt tris(*p*-bromophenyl)-aminium hexachloroantimonate in DCM solution at 0°C, a highly effective catalyst system for the hole-catalyzed Diels–Alder reaction, failed. Photosensitized single electron acceptor catalysis using *p*-dicyanobenzene in acetonitrile, another effective catalyst system for the Diels–Alder, also proved ineffective. Stirring **1** with 13X zeolites in DCM at ambient temperatures or in refluxing DCM also had no effect. However, when a solution of *threo* **1** in DCM containing 13X zeolites was irradiated with Pyrex-filtered UV light, smooth conversion to **2** was observed (54%). Control experiments revealed that in the absence of zeolites, **2** was not produced. Instead, **1** underwent photoequilibration of its Z and E geometric isomers. As a presumed consequence of similar photoequilibration of the product (**2**), a mixture of the geometric isomers of **2** was produced in the photoassisted, hole-catalyzed Cope reaction, thereby precluding determination of the stereochemistry (chair vs boat) of the hole-catalyzed Cope reaction. *Erythro* **1** was found to undergo the same reaction but at a much slower rate than the *threo* isomer.

In contrast, none of the methods mentioned above succeeded in catalyzing the Cope rearrangement of *meso*- or *dl*-3,4-diphenyl-1,5-hexadiene (**3**), *erythro*-1-(*p*-anisyl)-3,4-diphenyl-1,5-hexadiene (**4**), or *erythro*-2,3,4-triphenyl-1,5-hexadiene (**5**) (see Scheme 2). In the case of **3**, the starting



SCHEME 2

material was recovered unchanged in every instance. In the cases of **4** and **5**, decomposition of starting materials to unidentified substances, other than the Cope rearrangement products, was observed.

DISCUSSION

Previous research on zeolite-catalyzed Diels–Alder reactions has established the presence of mild hole-catalytic sites, especially on wide-pore zeolites such as those of the 13X type, which are capable of catalyzing cycloaddition reactions of some organic substrates having readily ionized conjugated systems (*11*). Like other forms of hole catalysis, zeolite catalysis appears to proceed via one-electron oxidation of the ionizable substrate to give the corresponding cation radical, which then undergoes extremely facile pericyclic reactions, including Diels–Alder cycloaddition. Subsequent to the pericyclic reaction involving the cation radical, back electron transfer to the product cation radical affords the neutral product molecule. Using the aminium salt and photosenitized electron transfer catalytic systems, a variety of conjugated dienes, styrenes, and electron-rich alkenes can be ionized and induced to undergo cycloadditions. In contrast, zeolite hole sites are observed to be much milder hole catalysts and thus far have been found to be effective with a narrower selection of conjugated substrates. In the case of styrenes, electron donor substituents such as *p*-anisyl were required for efficient zeolite-catalyzed cycloadditions. However, cycloadditions of simple styrenes could be accomplished using photoassisted zeolite catalysis (*11*). This procedure exploits the fact that the styrene moiety provides a chromophore which absorbs Pyrex-filtered UV light, thereby affording electronically excited styrenes which are much more readily ionized than their corresponding ground states. The equilibration of the Z and E geometric isomers of **1** by filtered UV light in the absence of zeolites confirms this general scenario, though no information is presently available on whether the light-absorbing molecule is in solution and must subsequently diffuse to the zeolite site or is absorbing directly from the zeolite site. In either case, formation of the cation radical of **1** ensues from donation of an electron from an excited state of **1** to a zeolite hole site. This species presumably has its cation radical character primarily located on the same styrene moiety which is the primary site of photoexcitation. Cope rearrangement of $\mathbf{1}^{+\cdot}$ then yields $\mathbf{2}^{+\cdot}$, the latter also presumably being a styrene-type cation radical. Back transfer to the zeolite (anion radical) site then affords neutral **2**.

The ineffectiveness of photoassistance in the attempted Cope rearrangement of **3** presumably results from the absence of a styrene-type chromophore or other chromophore which absorbs Pyrex-filtered UV light. In the case of **5**, the control run omitting the zeolites revealed a rapid photochemical transformation of the reactant, suggesting an excited state transformation which proceeds more rapidly than diffusion to the zeolite surface or, alternately, more rapidly than the Cope reaction of the cation radical ($\mathbf{5}^{+}$).

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REFERENCES

1. Evans, D. A., and Golob, A. M., *J. Amer. Chem. Soc.* **97**, 4765 (1975).
2. Yates, P., and Eaton, P., *Tetrahedron Lett.* **11**, 5 (1960).
3. Overman, L. E., and Knoll, F. M., *J. Amer. Chem. Soc.* **102**, 865 (1980).
4. Bellville, D. J., Wirth, D. W., and Bauld, N. L., *J. Amer. Chem. Soc.* **103**, 718 (1981).
5. Bellville, D. J., and Bauld, N. L., *J. Amer. Chem. Soc.* **104**, 2665 (1982).
6. Bellville, D. J., Pabon, R. A., and Bauld, N. L., *J. Amer. Chem. Soc.* **105**, 5158 (1983).
7. Libman, J., *J. Chem. Soc., Chem. Commun.*, 361 (1976).
8. Bauld, N. L., and Pabon, R. A., *J. Amer. Chem. Soc.* **105**, 633 (1983).

9. Bauld, N. L., Bellville, D. J., Pabon, R., Chelsky, R., and Green, G., *J. Amer. Chem. Soc.* **105,** 2378 (1983).
10. Bauld, N. L., Bellville, D. J., Gardner, S. A., Migron, Y., and Cogswell, G., *Tetrahedron Lett.* **8,** 825 (1982).
11. Bauld, N. L., and Ghosh, D., submitted for publication.
12. Cookson, R. C., Hughes, N. W., *J. Chem. Soc. Perkin Trans. 2,* 2738 (1973).

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