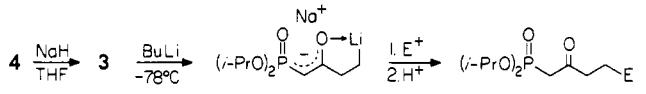
Table I

electrophile	product	yield, %[a]
CH_3OD	**7a**, E = D	70
CH_2=$CHCH_2Br$	**7b**, E = CH_2=$CHCH_2$	75
$CH_3CH_2CH_2I$	**7c**, E = $CH_3CH_2CH_2$	68
Me_3SiCl	**7d**, E = Me_3Si	70
Ph_2CO	**7e**, E = $Ph_2C(OH)$	72
CH_3CONMe_2	**7f**, E = CH_3CO	52

[a] Yields refer to pure product after purification on silica gel.

to the stabilization of the organolithium reagent via the intramolecular chelation of lithium by the enolate oxygen to form a five-membered cyclic structure (**6**).[13]

Phosphonate **4** is a stable compound[14] and was easily prepared in 75% yield by the reaction of diisopropyl lithiomethylphosphonate[2b,15] with methyl 3-(tri-*n*-butylstannyl)propionate.[16] The generation of **6** can be followed either by the disappearance

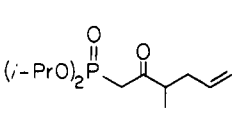


6 **7**

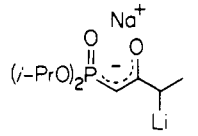
of the starting phosphonate (**4**) or by the appearance of tetrabutyltin after acid workup of the reaction aliquots. The transmetalation reaction is essentially complete within 5 min at −78 °C. Lithio compound **6** reacts with various electrophiles (Table I) exclusively at the δ carbon, giving rise to terminally substituted phosphonate esters **7**.[17]

The following experimental procedure is representative of the conversion. A dry 35-mL flask (equipped with a septum and a magnetic stirrer) containing 120 mg (2.5 mmol) of sodium hydride (50%, washed with hexanes to remove mineral oil) was flushed with argon and maintained under a positive pressure of argon. About 10 mL of freshly distilled dry THF was added, and then 1.05 g (2.0 mmol) of **4** was added dropwise. The reaction mixture was stirred at room temperature for 3 h to allow the formation of **3**. The reaction mixture was cooled to −78 °C, and 2.2 mmol (1.0 mL of a 2.2 M hexane solution) of *n*-butyllithium was added dropwise. The resulting light yellow solution was stirred at −78 °C for 10 min. The electrophile (2.2 mmol)[18] was added, and the reaction mixture was stirred at −78 °C for 15 min and at room temperature for 15 min. The reaction was quenched with 10% HCl (with dimethylacetamide as the electrophile, aqueous NH_4Cl was used), and the mixture was extracted with ethyl acetate. The crude product[19] was purified by either modified flash chromatography[20] or preparative thin-layer chromatography.

When the solution containing **6** (1,4-dianion) was stirred at 0 °C for 20 min, the solution turned red and on reaction with allyl bromide produced the γ-allyl compound (**8**) as the major product.



8



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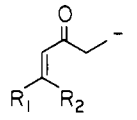

10

There was no evidence of **7b** being present in the product. This indicates that **6** is thermodynamically less stable and under conditions conducive to proton transfer gives rise to the more stable 1,3-dianion (**9**).

The generation of **6** shows for the first time that it is possible to generate a homoenolate anion equivalent by tin/lithium exchange when the carbonyl group is protected electronically from nucleophilic attack by butyllithium. The successful transformations reported here, in conjunction with the known reactions of β-ketophosphonates, allow the use of stannane **4** as a synthon for β′-substituted α,β-enones (**10**). The use of **6** to synthesize biologically useful organic molecules and the generation of similar δ-lithio derivatives of other functionalized systems[21] are being investigated.

Acknowledgment. I thank Dr. T. H. Whitesides for helpful discussions.

(13) This kind of intramolecular chelated structure of organolithium reagents has been postulated in many cases: (a) Klumpp, G. W.; Kool, M.; Schakel, M.; Schmitz, R. F.; Boutkan, C. *J. Am. Chem. Soc.* **1979**, *101*, 7065. (b) Marino, J. P.; Kostusyk, J. L. *Tetrahedron Lett.* **1979**, 2489. (c) Beak, P.; McKinnie, B. G. *J. Am. Chem. Soc.* **1977**, *99*, 5213. (d) Still, W. C.; Macdonald, T. L. *Ibid.* **1974**, *96*, 5561. (e) Hartmann, J.; Stähle, M.; Schlosser, M. *Synthesis* **1974**, 888. (f) House, H. O.; Bare, T. M.; Hanners, W. E. *J. Org. Chem.* **1969**, *34*, 2209.

(14) Carbonyl compounds containing the trialkyltin group at the β position are usually stable to moisture and treatment with alkali.

(15) Ford-Moore, A. H.; Williams, J. H. *J. Chem. Soc.* **1947**, 1465.

(16) VanDerKerk, G. J. M.; Noltes, J. G.; Luijten, J. G. A. *J. Appl. Chem.* **1957**, *7*, 356.

(17) Yields have not been optimized. In most reactions, 10–20% of protonated compound **7** (E = H) was isolated as the byproduct. As expected, γ-hydroxy ketone **7e** exists predominantly in the cyclic hemiketal structure: Kyrides, L. P.; Zienty, F. B. *J. Am. Chem. Soc.* **1946**, *68*, 1385. The ^1H NMR, IR, and analytical data of all compounds were in accord with the assigned structures.

(18) Excess chlorotrimethylsilane (5.2 mmol) was used for the preparation of **7d**.

(19) The crude residue can be partly purified by partitioning between acetonitrile and hexanes; see: Berge, J. M.; Roberts, S. M. *Synthesis* **1979**, 471.

(20) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(21) Preliminary experiments show that it is possible to generate PH_3P^+–$^-CHCOCH_2CH_2Li$ similarly. This work will soon be submitted for publication.

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The First Practical Method for Asymmetric Epoxidation

Sir:

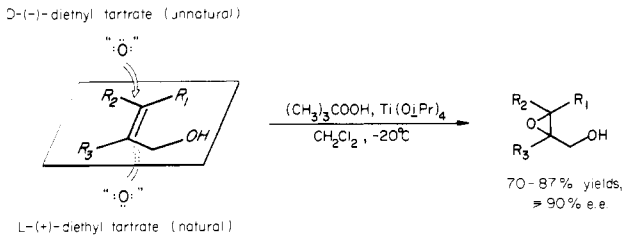
As revealed in Scheme I, we have discovered a new metal-catalyzed asymmetric epoxidation process which is far more selective than any of the previously described methods[1] for this type of asymmetric transformation. The simplicity of this new method is one of its more attractive aspects; the necessary components [(+) or (−)-diethyl tartrate,[2] titanium tetraisopropoxide, and

(1) (a) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, NJ, 1971, pp 258-62; (b) S. Yamada, T. Mashiko, and S. Terashima, *J. Am. Chem. Soc.*, **99**, 1988 (1977); (c) R. C. Michaelson, R. E. Palermo, and K. B. Sharpless, *ibid.*, **99**, 1990 (1977); (d) H. B. Kagan, H. Mimoun, C. Mark, and V. Schurig, *Angew. Chem., Int. Ed. Engl.*, **18**, 485 (1979) [records the highest ee (35%) for a hydrocarbon olefin]; (e) K. Tani, M. Hanafusa, and S. Otsuka, *Tetrahedron Lett.*, 3017 (1979); (f) H. Wynberg and B. Marsman, *J. Org. Chem.*, **45**, 158 (1980); (g) K. Takai, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 1659 (1980); (h) J. Rebek, *Heterocycles*, in press.

(2) We had earlier examined the effect of chiral alcohols and chiral diols (including L(+)-diethyl tartrate) on the molybdenum- and vanadium-catalyzed TBHP epoxidation of isolated olefins as well as of allylic alcohols. Small (i.e., <10% ee) asymmetric inductions were noted, but they were not deemed worth reporting: R. C. Michaelson and K. B. Sharpless, unpublished results, Massachusetts Institute of Technology, 1974. Otsuka and co-workers have recently described[1e] low (<11% ee) asymmetric inductions in the epoxidation of hydrocarbon olefins with TBHP in the presence of dialkyl tartrate esters and a molybdenum(VI) catalyst.

0002-7863/80/1502-5974$01.00/0

Scheme I



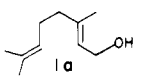
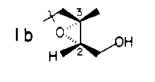
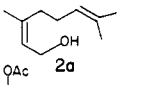
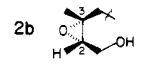
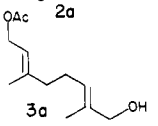
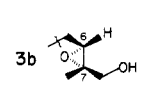
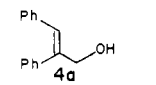
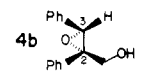
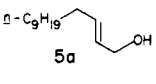
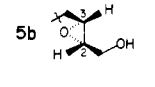
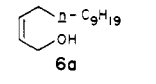
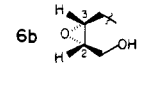
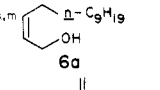
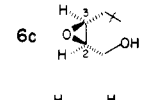
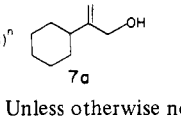
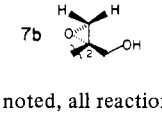
tert-butyl hydroperoxide] are all[3] commercially available at low to moderate cost.[4]

This new chiral epoxidation system possesses two especially striking features. First, it gives uniformly high asymmetric inductions throughout a range of substitution patterns[5,17] in the allylic alcohol substrate (Table I). Second, upon use of a given tartrate enantiomer, the system seems obliged to deliver the epoxide oxygen from the same enantioface of the olefin regardless of the substitution pattern. This latter characteristic is highlighted in Scheme I: when the olefinic unit is in the plane of the drawing with the hydroxymethyl substituent at the lower right as shown, the use of (+)-diethyl tartrate leads to addition of the epoxide oxygen from the bottom. Of course, when (−)-diethyl tartrate is employed, the epoxide oxygen is added from the top.

A 500-mL, 1-neck round-bottom flask equipped with a Teflon-coated magnetic stir bar was oven dried and then fitted with a serum cap and flushed with nitrogen. The flask was charged with 200 mL of dry (distilled from CaH_2) reagent-grade dichloromethane and cooled by stirring in a −23 °C bath (dry ice/CCl_4).[6] Then the following liquids were added sequentially via syringe while stirring in the cooling bath: 5.94 mL (5.68 g, 20 mmol) of titanium tetraisopropoxide (Aldrich); 3.43 mL (4.12 g, 20 mmol)[7] of L(+)-diethyl tartrate (used as received from Aldrich), stirred 5 min before next addition; 3.47 mL (3.08 g, 20 mmol) of geraniol (Aldrich Gold Label); and, finally, ca. 11 mL of a dichloromethane solution (3.67 M in TBHP) containing ca. 40 mmol (2 equiv) of anhydrous *tert*-butyl hydroperoxide (TBHP). (One can just as well use dichloroethane or carbon tetrachloride solutions of anhydrous TBHP. Complete experimental details for preparing these anhydrous TBHP solutions are given elsewhere.[8])

The resulting homogeneous solution was then stored overnight (ca. 18 h) in the freezer at ca. −20 °C in the sealed (serum cap) reaction vessel (the progress of the epoxidation can be monitored by TLC). Then the flask was placed in a −23 °C bath (dry

Table I. Asymmetric Epoxidation of Allylic Alcohols[a]

	Allylic Alcohol	Epoxyalcohol	% yield[b]	% e.e.[c]	Configuration[d]
(1)	 1a	1b 	77	95 (Eu, M)	2(S), 3(S)[e]
(2)	 2a	2b 	79	94 (Eu, M)	2(S), 3(R)[f]
(3)	 3a	3b 	70[g]	>95 (Eu)	6(S), 7(S)[g]
(4)[h]	 4a	4b 	87	>95 (Eu)	2(S), 3(S)[i]
(5)	 5a	5b 	79	>95 (M)	2(S), 3(S)[j]
(6)[k]	 6a	6b 	82	90 (M)	2(S), 3(R)[l]
(7)[k,m]	 6a	6c 	80	90 (M)	2(R), 3(S)[m]
(8)[n]	 7a	7b 	81	>95 (M)	2(S)[o]

[a] Unless otherwise noted, all reactions were performed as described in detail for geraniol (**1a**). In most cases, the scale was smaller (ca. 2 mmol). [b] Isolated yields. All new compounds gave appropriate analytical and spectral data. [c] The enantiomeric excesses were determined by ^1H NMR on the corresponding epoxy acetates (pyridine/Ac_2O) in the presence of $Eu(hfbc)_3$ and/or by conversion to the MTPA ester followed by ^1H or ^{19}F NMR analysis. The technique(s) used is(are) indicated in parentheses. When both methods were employed, the % ee reported was an average of the two values. [d] All absolute configurations were proven by chemical correlation as indicated for each case. All of the epoxy alcohols in the table gave a negative rotation in $CHCl_3$ except for **4b** and **6c**. [e] The enantiomer of **1b** has been correlated with (*R*)-(−)-linalool.[1b] [f] The enantiomer of **2b** has been correlated with (*S*)-(+)-linalool.[1b] [g] The alkaline hydrolysis step was omitted in this case; the diethyl tartrate was removed by chromatography. 6(*S*),7(*S*)-(−)-**3b** was correlated with (*S*)-(−)-6,7-epoxygeraniol [S. Yamada, N. Oh-hashi, and K. Achiwa, *Tetrahedron Lett.*, 2557 (1976)]. The 8-hydroxyl group of **3b** was replaced by hydrogen via the following reaction sequence: TsCl/pyridine; NaI/acetone; NaH_3BCN/HMPA; LiOH/CH_3OH, H_2O. [h] Epoxidation was performed at 0 °C and was complete in less than 30 min. [i] Coworker Victor S. Martin (unpublished results) has correlated **4b** with methyl (*S*)-(+)-2,3-diphenyl-2-hydroxypropionate (ii) [H. R. Sullivan, J. R. Beck, and A. Pohland, *J. Org. Chem.*, **28**, 2381 (1963); see also: E. Bye, *Acta Chem. Scand.*, **27**, 3403 (1973)]. Epoxy alcohol **4b** was transformed to ii by the following steps: RuO_4/CCl_4, CH_3CN, H_2O; CH_2N_2/Et_2O; W-2 Raney nickel, H_2/absolute EtOH. [j] **5b** was correlated with (*R*)-(−)-tridecan-3-ol (K. Freudenberg, Stereochemie. Eine Zusammenfassung der Ergebnisse, Grundlagen und Probleme, Franz Deuticke, Ed., Leipzig und Wien, p 696) by the following sequence: TsCl/pyridine; NaI/acetone; Zn/HOAc; H_2/PtO_2. [k] These results were obtained by B. E. Rossiter during enantioselective syntheses of both natural (+)- and unnatural (−)-disparlure (B. E. Rossiter and K. B. Sharpless, unpublished results). [l] **6b** was correlated with unnatural (−)-disparlure (unpublished results, see ref *k* above). [m] In this case, D(−)-diethyl tartrate (the unnatural enantiomer) was used. **6c** was correlated with natural (+)-disparlure (unpublished results, see ref *k* above). [n] This epoxidation was run for 40 h at −20 °C, and a trace of **7a** still remained. [o] **7b** was correlated with (*R*)-(−)-2-cyclohexyl-2-butanol [D. J. Cram and J. Tadanier, *J. Am. Chem. Soc.*, **81**, 2737 (1959)] through the following steps: $LiAlH_4/Et_2O$; TsCl/pyridine; $LiCuMe_2/Et_2O$.

(3) The diethyl ester of unnatural (−)-tartaric acid has recently become available from Aldrich.

(4) Unnatural D(−)-tartaric acid costs about 34 times more than natural L(+)-tartaric acid when both are purchased in 100-kg quantities; see note 5: E. Hungerbühler, D. Seebach, and D. Wasmuth, *Angew. Chem., Int. Ed. Engl.*, **18**, 958 (1979). This makes it by far the most expensive component since the other three are all available for a few dollars a pound, even in research quantities.

(5) Five of the eight possible basic substitution patterns for a primary allylic alcohol are represented in Table I. We plan to examine the three remaining types, but based on the existing cases no surprises (low ee and/or change in enantioselection pattern) are expected.

(6) Cooling serves two purposes, the obvious one of optimizing enantioselectivity, and the less obvious one of minimizing transesterification processes. Titanium alkoxides are excellent transesterification catalysts, and there is an extensive patent literature on this subject. We have now found that the rate of transesterification is substantially accelerated by an α-hydroxy substituent. Thus, in the presence of $Ti(O\text{-}i\text{-}Pr)_4$, ethyl mandelate transesterifies much faster than methyl phenylacetate (P. H. J. Carlsen and K. B. Sharpless, unpublished results). As α-hydroxy esters, the tartrates also undergo rather facile transesterification in our reaction system at room temperature. This produces tartrate esters which incorporate 2-propanol and also the allylic alcohol substrate, and gives rise to a multitude of problems at the product isolation stage. Fortunately, transesterification is slow at −20 °C, and running the reactions near that temperature has so far proved a viable solution to the problem. However, other solutions are being sought.[15]

(7) It is important to have at least 1 mol of tartrate per mol of $Ti(OR)_4$. A slight excess of tartrate does not seem to matter, so we sometimes add a small excess (2–5%) to be safe. This consideration is more important for small-scale reactions where it is difficult to measure reagents accurately.

(8) K. B. Sharpless and T. R. Verhoeven, *Aldrichimica Acta*, **12**, 63 (1979). This article also contains the best previous result (80% ee) for asymmetric epoxidation of an allylic alcohol (see eq 32, p 67).

ice/CCl_4) and 50 mL of 10% aqueous tartaric acid solution was added while stirring; the aqueous layer solidified. After 30 min, the cooling bath was removed and stirring was continued at room temperature for 1 h or until the aqueous layer became clear. After separation of the aqueous layer, the organic layer was washed once with water,[9] dried (Na_2SO_4), and concentrated to afford a colorless oil with an odor revealing contamination by TBHP.[9]

This oil was diluted with 150 mL of ether, and the resulting solution was cooled in an ice bath, and then 60 mL of 1 N sodium hydroxide solution was added. This produced a two-phase mixture which was stirred at 0 °C for $^1/_2$ h.[10] The ether phase was washed with brine, dried (Na_2SO_4), and concentrated to give 4.24 g of a clear oil. Chromatography on silica gel afforded 2.6 g (77%) of 2(*S*),3(*S*)-epoxygeraniol, $[\alpha]^{24}_D$ -6.36° (*c* 1.5, $CHCl_3$). Analysis of this material as the MTPA ester[11] gave an enantiomeric excess (ee) of >95% whereas analysis of the derived epoxy acetate by using Eu(hfbc)$_3$ chiral shift reagent gave 94% ee.

The "typical procedure" given for geraniol has a limitation which is important to emphasize. *Very poor yields are realized if the epoxy alcohol produced is fairly water soluble.* For example, although allyl alcohol and crotyl alcohol are epoxidized by this system, it is difficult to extract (even with "salting-out" techniques) more than 10–30% of the intact epoxy alcohol product. We are working on solutions to the isolation problems presented by these and related cases.

The procedure described above for epoxidation of geraniol calls for 1 equiv of both titanium isopropoxide and diethyl tartrate. This is by no means necessary in all cases. With reactive allylic alcohols (**1a**, **2a**, **3a**, and **4a** in Table I), a catalytic amount (e.g., 0.1 equiv) of both Ti(O-*i*-Pr)$_4$ and diethyl tartrate suffices[12] under otherwise identical reaction conditions. However, for the less-reactive substrates in Table I (**5a**, **6a**, and **7a**), the "1-equiv" conditions described above were necessary to achieve reasonable reaction rates. Even under the "1-equiv" conditions, allylic alcohol **7a** required almost 2 days to approach completion. For this first report, the most general method (stoichiometric amount of the chiral catalyst system) was chosen for presentation. The catalytic system (which has some important advantages[13] in addition to the obvious ones) is under further study.

Many other aspects of this unique epoxidation system are also being investigated in our laboratory. Of foremost interest is a good mechanistic rationale for the remarkable selectivities which are seen. Our approach to the mechanism involves both kinetic studies and structural modifications of the chiral ligand. From a synthetic point of view, there are several interesting further developments, among them: (1) this same epoxidation system is effective for the kinetic resolution of racemic allylic alcohols,[14] and (2) predominant inversion of the enantioselectivity pattern shown in Scheme I is observed with certain minor structural modifications of the chiral tartrate ligand.[15] We are also extending our studies to include homo- and bishomoallylic alcohols, and β-hydroxy sulfides.

To the best of our knowledge, this new enantioselective, catalytic process is discriminating to a degree barely[16] rivaled by any other nonenzymatic catalytic process. In its promiscuous acceptance of varied allylic alcohol substrates,[5] it also has some desirable features which would be difficult for even an enzymatic catalyst to achieve.[17]

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(9) Due to the small scale, we have chosen to ignore the excess TBHP. If one wishes to remove it, a number of reductive procedures are available.[8]

(10) Do not expose the reaction mixture to this base treatment for longer than $^1/_2$ h as base-catalyzed rearrangements of the epoxy alcohol may occur: G. B. Payne, *J. Org. Chem.*, **27**, 3819 (1962). Diethyl tartrate is fairly soluble in water and hydrolyzes readily under these conditions. We have found that (+)-dimethyl tartrate (Aldrich) is as effective (>95% ee) as the ethyl ester for epoxidation of **4a**. The methyl ester is much more water soluble and may prove advantageous when the hydrolysis step is unacceptable. The isopropyl ester also works well, but leads to increased trouble at the workup stage.

(11) J. A. Dale, D. L. Dull, and H. S. Mosher, *J. Org. Chem.*, **34**, 2543 (1969). We used MTPA chloride and DMAP in CH_2Cl_2.

(12) Under these catalytic conditions, (0.1 equiv of Ti(OR)$_4$/DET), the yields of **1b**, **2b**, and **4b** were comparable to or somewhat better than those with 1 equiv, and the product isolations were cleaner and easier. The enantiomeric excess was somewhat poorer for **1b** (91% ee) and **2b** (84% ee) but was still >95% ee for **4b**.

(13) The possibilities for product stability problems, transesterification problems, and most other workup and isolation problems are greatly diminished.

(14) M. Ikeda, Y. Yamada, T. Katsuki, V. S. Martin, and K. B. Sharpless, unpublished results.

(15) J. Ryan Zilenovski and K. B. Sharpless, unpublished results.

(16) Asymmetric catalytic hydrogenations can be extremely enantioselective; for an example of 100% ee, see: M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6262 (1977). However, these asymmetric hydrogenation processes appear more sensitive to permutation of the olefin substitution patterns than does the asymmetric epoxidation process we have described here.

(17) **Note Added in Proof.** We now have results for two more of the basic substitution patterns of primary allylic alcohols (see note 5). Allyl alcohol itself affords 2(*S*)-glycidol, ca. 15% yield, 73% ee [performed at 0 °C by using (+)-diisopropyl tartrate and Ti(OiPr)$_4$]; the higher temperature probably contributes to the lower ee observed in this case. (*Z*)-2-Methylhept-2-enol gives the 2(*S*),3(*R*)-epoxy alcohol, 80% yield, 89% ee [performed at -20 °C, using (+)-diethyl tartrate and Ti(OiPr)$_4$]. Thus, both conform to the rules stated in paragraph two and only the tetrasubstituted type of primary allylic alcohol remains to be tried.

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2,3-Di-*n*-propyl-1,4-dehydrobenzene

Sir:

Rearrangement and trapping studies[1] have implicated an "open" or biradical form (**2**) of 1,4-dehydrobenzene as an intermediate in the thermal reaction of (*Z*)-hexa-1,5-diyn-3-ene (**1**, R = H; Scheme I). Attempts to obtain kinetic evidence for the existence of a true intermediate in this reaction, however, have been frustrated by the low yield of aromatic products obtained in solution pyrolyses of several compounds of type **1**. In this paper, we report a detailed study of the thermolysis of (*Z*)-4,5-diethynyl-4-octene (**4**).[2] This reaction gives high yields of products formed by rearrangement and intramolecular and intermolecular trapping of the intermediate 1,4-dehydrobenzene **5**. The kinetics of the solution pyrolysis of **4** in the presence and absence of trapping agent establish that the 1,4-dehydrobenzene is a discrete intermediate on the pathway leading to products. By following this reaction in the probe of an NMR spectrometer at high temperature, we have, for the first time, observed CIDNP in a 1,4-dehydrobenzene reaction. This observation, along with kinetic and chemical trapping evidence, indicates the subsequent formation of two additional intermediates on the pathway to products. The observation of CIDNP, coupled with the reactivity exhibited by **5** and the other two intermediates, implicates a biradical description of these molecules.

(1) (a) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660. (b) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25. (c) Johnson, G. C.; Stofko, J. J.; Lockhart, T. P.; Brown, D. W.; Bergman, R. G. *J. Org. Chem.* **1979**, *44*, 4215. See also, however: (d) Breslow, R.; Napierski, J.; Clarke, T. C. *J. Am. Chem. Soc.* **1976**, *98*, 570. (e) Breslow, R.; Khanna, P. L. *Tetrahedron Lett.* **1977**, 3429.

(2) Details of the synthesis of compound **4** will be presented in a full paper.

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