produced no detectable amounts of CH_4 after several days. Similarly, mixtures containing only methyl iodide and ethylenediamine produced no methane. The reactions with methyl bromide and methyl chloride were carried out in an analogous fashion, except that these gases were introduced into the reaction flask from calibrated Pyrex bulbs. The reaction times were extended to 24 h or longer in order to accommodate the lower reactivity of these halides.

Thermal Reaction of Triphenyltin Hydride with Methyl Iodide. A cylindrical reaction tube equipped with a Teflon covered stirrer was attached to a vacuum line and flame dried. A 0.20-mL aliquot of a 0.2 M hexane solution of Ph_3SnH was added to the cooled tube under a stream of argon. The contents of the reaction tube were deoxygenated by means of three freeze–pump–thaw cycles. A weighed amount of methyl iodide was distilled into the tube, and the flask was sealed under vacuum. The reaction mixture was stirred in the dark at 0 °C for 24 h. The flask was then attached to a combustion line and the methane was removed and converted to carbon dioxide for isotopic analysis.

Photochemical Reactions of Triphenyltin Hydride with MeX (X = I, Br, Cl). A cylindrical reaction tube equipped with a Teflon covered stirrer was attached to a vacuum line and flame dried. After the flask had cooled, 0.40 to 0.50 mL of a 7.0×10^{-2} M hexane solution of Ph_3SnH and 3.0 mL of hexane were added under a stream of argon. The contents was thoroughly deoxygenated by freeze–pump–thaw cycles. A weighed amount of methyl iodide was distilled into the flask, and the flask was sealed in vacuo. The flask was placed in a 0 °C bath contained within the photolysis chamber (Rayonet photochemical reactor, Southern N.E. Ultraviolet Co., Middletown, CT) and thermally equilibrated for 10 min. The rapidly stirred solution was irradiated for 60 s with lamps nominally emitting at 350 nm. The methane was transferred to a combustion vacuum line by means of a Toepler pump and analyzed in the usual manner. The reactions involving methyl bromide and methyl chloride were prepared in an analogous fashion, except these gases were introduced with the aid of calibrated Pyrex bulbs. The conditions for the photolysis of methyl bromide were similar to those employed for methyl iodide. However, the reactions of methyl chloride required more concentrated solutions and longer periods of irradiation. Photolysis of methyl iodide in the absence of Ph_3SnH produced less than 5.0×10^{-5} mmol of methane under these experimental conditions.

Acknowledgment. We thank Dr. John M. Hayes for his helpful interest, the National Institutes of Health (General Medical Sciences), the National Science Foundation, and the National Aeronautics and Space Administration for financial assistance.

Registry No. Methyl bromide, 74-83-9; methane, 74-82-8; methyl iodide, 74-88-4; methyl chloride, 74-87-3; chromium(II) triflate, 58164-61-7; triphenyltin hydride, 892-20-6; $en_2Cr(II)$, 15525-39-0; $Ph_3Sn(III)$, 14971-33-6.

Supplementary Material Available: A complete listing of kinetic isotope effects at various conversions of methyl iodide, bromide, and chloride with Ph_3SnH and $en_2Cr(II)$ (4 pages). Ordering information is given on any current masthead page.

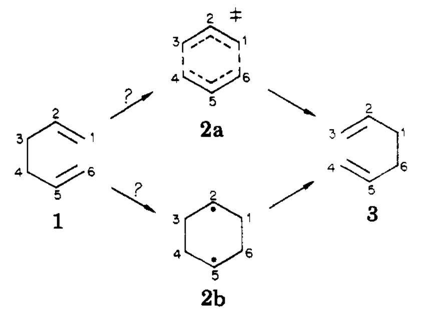
Kinetics of the Cope Rearrangement of a 3,4-Diphenylhexa-1,5-diene

Raymond P. Lutz* and Harlan A. J. Berg

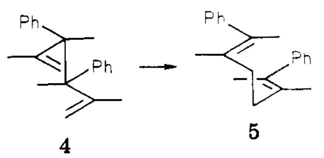
Department of Chemistry, Portland State University, Portland, Oregon 97207

Received April 15, 1980

The mechanism of the thermal Cope rearrangement has generally been conceived as a concerted process (1 → 2a → 3), designated at one time as a "no mechanism" reaction, and later labeled as an allowed [3,3] sigmatropic shift.[1] However, the possible intervention of a cyclohexane-1,4-diyl intermediate (2b) was recognized early on[2] and recently received experimental support from the work of Dewar and Wade,[3] who established that phenyl substituents in the 2- or 2,5- positions, a substitution pattern which should promote stabilization of the radical centers of a species such as 2b, did indeed lead to significant rate enhancement in the Cope rearrangement. Dewar and Wade determined kinetic parameters for the 2-phenyl-, 3-phenyl-, 2,4-diphenyl- and 2,5-diphenylhexa-1,5-dienes for comparison with the parent hexa-1,5-diene. In view of the significance of the phenyl-substituted substrates in defining the emerging picture of the Cope rearrangement mechanism, we complete the series by reporting our kinetic parameters for the Cope rearrangement of *dl*-3,4-diphenylhexa-1,5-diene (4),[4] a substrate with both phenyl groups positioned in such a way as to preclude participation in cyclohexane-1,4-diyl delocalization.



We had established earlier that 4 rearranges cleanly through a chair-like transition state, yielding exclusively *trans,trans*-1,6-diphenylhexa-1,5-diene (5) as the kinetically controlled product.[5] The pseudoequatorial disposition of phenyl groups in the transition state derived from 4 allows electronic interaction with the phenyl groups with minimal complications by steric effects.



First-order rate constants at three temperatures were determined in *n*-heptane, with product formation monitored by the increase in UV absorption. Values are summarized in Table I, along with Arrhenius activation parameters; these lead to $\Delta H^* = 24.0 \pm 0.2$ kcal/mol and $\Delta S^* = -12.4 \pm 0.6$ eu. Significant rate enhancement by the phenyl groups in this system can be seen by comparison with the parent hexa-1,5-diene, where $E = 34.3$ kcal/mol, $\log A = 10.36$, $\Delta H^* = 33.5$ kcal/mol, and $\Delta S^* = -13.8$ eu.[2c] Activation by unsaturated substituents in the 3 and/or 4 positions is typical for Cope rearrangements and is usually interpreted as stabilization of a transition state resembling a pair of weakly interacting allyl radicals (2a). Rate enhancement in 4 is roughly equivalent to that observed for

---

(1) For a recent review, see S. J. Rhoads and N. R. Raulins, *Org. React.*, **22**, 1 (1975).

(2) (a) C. A. Grob, H. Link, and P. W. Schiess, *Helv. Chim. Acta*, **46**, 483 (1963); (b) N. C. Deno, private communication, 1964; (c) W. von E. Doering, V. G. Toscano, and G. H. Beasley, *Tetrahedron*, **27**, 5299 (1971).

(3) M. J. S. Dewar and L. E. Wade, *J. Am. Chem. Soc.*, **95**, 290 (1973); **99**, 4417 (1977). (b) For a comparable effect with cyano and methoxycarbonyl groups, see R. Wehrli, H. Schmid, D. E. Bellus, and H.-J. Hansen, *Helv. Chim. Acta*, **60**, 1325 (1977).

(4) H. A. J. Berg, Master's Thesis, Portland State University, Portland, OR, 1972.

(5) R. P. Lutz, S. Bernal, R. J. Boggio, R. O. Harris, and M. W. McNicholas, *J. Am. Chem. Soc.*, **93**, 3985 (1971).

0022-3263/80/1945-3915$01.00/0

Table I. Rearrangement of *dl*-3,4-Diphenylhexa-1,5-diene in *n*-Heptane (5×10^{-5} M)[a]

temp, °C	10^4k, s^{-1} [b]	E, kcal/mol[c]	log A[c]
90.0	0.540 ± 0.003	24.7 ± 0.2	10.6 ± 0.1
100.0	1.37 ± 0.003		
109.9	3.32 ± 0.01		

[a] Uncertainties are standard deviations. [b] First-order rate constants (weighted means). [c] Arrhenius parameters.

Table II. First-Order Rate Constants for Rearrangement of 4[a]

temp, °C	10^4k, s^{-1}
90.03	0.535 ± 0.007
90.03	0.541 ± 0.004
89.90	0.545 ± 0.003
100.01	1.33 ± 0.02
100.02	1.38[b] ± 0.004
100.02	1.36 ± 0.01
100.02	1.38[c] ± 0.02
100.02	1.38 ± 0.03
109.90	3.33 ± 0.01
109.90	3.17 ± 0.03
109.89	3.14[d] ± 0.05

[a] Uncertainties are standard deviations. [b] Samples contained 5×10^{-8} M *N*-phenyl-β-naphthylamine free-radical inhibitor. [c] Samples contained 5×10^{-7} M *N*-phenyl-β-naphthylamine. [d] Surface-to-volume ratio increased 8-fold.

2,5-diphenylhexa-1,5-diene rearrangement in *o*-dichlorobenzene ($E = 21.9$ kcal/mol, $\log A = 8.86$). The most direct comparison is between the rate constant at 100.0 °C reported above for 4 and the observed $k = 2.85 \times 10^{-4}$ s^{-1} at 100.95 °C for the 2,5 derivative. The effect of solvent differences is such that the 3,4 derivative would probably have the larger rate constant if measurements were made in the same solvent.[6]

Activation by unsaturated substituents in the 3 and/or 4 as well as the 2 and/or 5 positions in Cope substrates can be accounted for by a spectrum of transition states influenced by the substitution pattern.[7] One component of the spectrum is approximated by the bonding in cyclohexane-1,4-diyl, another by a pair of interacting allyl radicals.

Experimental Section

Replicate kinetic measurements were carried out on ca. 5×10^{-5} M *n*-heptane solutions of 4 in sealed evacuated Pyrex ampules in a thermostatted oil bath. Thermometers were calibrated against NBS standards. Ampules were withdrawn periodically and the contents were analyzed directly with a Cary 14 recording ultraviolet spectrophotometer. Relative concentrations of starting and rearranged diene were calculated from absorbance measurements at 256 nm.

Since product decomposition became perceptible after about 85% reaction, rate constants were obtained from data points obtained up to three half-lives (generally ten ampules). Excellent first-order plots were observed, with rate constants calculated by standard least-squares methods. The reaction was found to be homogeneous, in that eightfold increase in the surface-to-volume ratio had a negligible effect on the reaction rate at 110 °C. VPC analysis[5] of the product of rearrangement of 4 at 110 °C for 12 h (20 half-lives) in dilute *n*-heptane in a sealed, evacuated ampule indicated >99.9% 5.

Activation parameters were calculated from the observed rate constants as given in Table II. Weighted means[8] are given in Table I.

Registry No. 4, 74467-15-5; 5, 58463-02-8.

---

[6] The Cope rearrangement of 3-phenylhexa-1,5-diene at 190 °C is about four times faster in *o*-dichlorobenzene than in the gas phase (ref 3a).

[7] (a) J. J. Gajewski and N. D. Conrad, *J. Am. Chem. Soc.*, **101**, 6693 (1979); (b) R. Wehrli, D. Bellus, H.-J. Hansen, and H. Schmid, *Chimia*, **30**, 416 (1976).

[8] C. L. Perrin, "Mathematics for Chemists", Wiley-Interscience, New York, 1970, p 159.

A Particularly Convenient Preparation of Benzohydroximinoyl Chlorides (Nitrile Oxide Precursors)

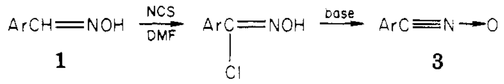
Kou-Chang Liu,*[†] Becky R. Shelton, and Robert K. Howe*

Research Department, Monsanto Agricultural Products Company, St. Louis, Missouri 63166

Received April 15, 1980

Nitrile oxides have found extensive utility in preparation of heterocycles via 1,3-dipolar cycloadditions.[1,2] Benzohydroximinoyl chlorides (2) are especially useful, stable, storable precursors of the relatively unstable benzonitrile oxides (3), which tend to dimerize within a few minutes to several days.[2] The most widely employed method of preparation of 2 is chlorination of oximes with chlorine gas; however, chlorine gas is hazardous and ring chlorination occurs with benzaldehyde oximes that contain electron-donating substitutents.[3,4]

We have found that *N-chlorosuccinimide (NCS) in DMF*[5,6] *provides a particularly selective and by far the most convenient method of preparation of 2.* Yields are excellent (see Table I). The crude products are almost invariably sufficiently pure to be employed without purification for nitrile oxide reactions. The experimental procedure is quite simple and suitable for large-scale preparations. NCS is a solid and thus is easy to handle and to measure accurately. Ring chlorination occurs only with very strongly activated aromatic rings.



$$\underset{\mathbf{1}}{\mathrm{ArCH{=}NOH}} \xrightarrow[\mathrm{DMF}]{\mathrm{NCS}} \underset{\mathbf{2}}{\mathrm{Ar}\underset{\mathrm{Cl}}{\mathrm{C}}\mathrm{{=}NOH}} \xrightarrow{\mathrm{base}} \underset{\mathbf{3}}{\mathrm{ArC{\equiv}N{\rightarrow}O}}$$

Mesitaldehyde oxime could not be chlorinated by any of the previously known procedures without ring chlorination.[7] Treatment of mesitaldehyde oxime with exactly 1 equiv of NCS in DMF gave fairly pure mesitohydroximinoyl chloride in 92% yield, without any purification. The product contained no detectable ring-chlorinated material (NMR analysis of hydroximinoyl chloride and GC analysis of derived nitrile oxide) and gave pure mesitonitrile oxide, mp 110–112 °C (lit.[7] mp 110–112 °C), in 95% yield upon treatment with triethylamine in ether.

Previous attempts[4,8] to prepare 2-methoxybenzohydroximinoyl chloride by chlorination of 2-methoxybenzaldehyde oxime with chlorine in various solvents were unsuccessful; ring-chlorinated products were obtained in each case. Use of NCS in DMF gave 2-methoxybenzohydroximinoyl chloride in 92% yield, with no detectable ring chlorination (NMR analysis).

The very strongly activated 2,4-dimethoxybenzaldehyde oxime reacted with NCS in DMF to give a mixture of products, in 92% yield, of which two-thirds was 5-chloro-2,4-dimethoxybenzaldehyde oxime from ring chlo-

---

[†] Research Center, GAF Co., Wayne, NJ 07470.