Thermodynamic and Kinetic Secondary Isotope Effects in the Cope Rearrangement

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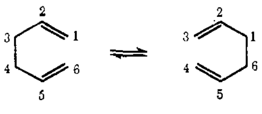
Abstract: Secondary α-deuterium isotope effects are shown to be a nonlinear function of the location of the transition state on the reaction coordinate. Thermodynamic and kinetic deuterium isotope effects on the thermal rearrangement of 1,5-hexadienes **1a** and **1b** and 3,3-dicyano-2-ethyl-1-methyl-1,5-hexadienes **2a** and **2b** have been determined. The isotope effect on the equilibrium constant for **1a** $\rightleftharpoons$ **1b** (1.10/atom D) gives a measure of the isotopic fractionation factor for hydrogen between an sp^3 and sp^2 hybridized carbon where a carbon–carbon bond is cleaved. The kinetic effects on the rearrangement of **2a** and **2b** are shown to be the same as the thermodynamic effects on the bond-breaking side (k_H/k_D 1.1), but only a fourth as large (k_H/k_D 0.97/atom D) on the bond-making side. This is only consistent with a relation between structure and isotope effects such as that shown in Figure 1.

The usefulness of secondary isotope effects in reaction mechanism studies seems to be well established.[2] Thus, α-effects have been used as supporting evidence for the limiting character of solvolytic reactions,[3] while β effects offered information about charge delocalization and conformation in the activated complex.[3,4] However, with few exceptions, these studies yielded no new information about the nature and behavior of secondary isotope effects. They were rationalized[5] in terms of rehybridization, hyperconjugation, or similar phenomena but little effort was spent to investigate systematically why the magnitude of these effects sometimes differs by few per cent for no apparent reason at all, while in the other cases effects might be expected but are not found.

Some time ago,[6] we started studies in this direction and one of the possible approaches was to look at the isotope effects in equilibria and in reactions which can be taken as mechanistically unambiguous. Since it was desirable to avoid any solvent effects and if possible also electronic effects, the choice fell on the Cope rearrangement.[7] The results of these studies are presented in this paper.

The systems chosen were (a) biallyl (**1**) and (b) 3,3-dicyano-2-ethyl-1-methyl-1,5-hexadiene (**2**).



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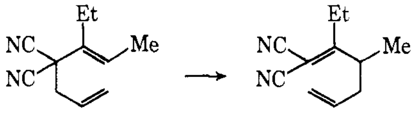
Rearrangement of **1** represents a degenerate reaction which can be detected only by proper labeling. For our purpose **1** was labeled with deuterium at either vinyl carbons 1 and 6 or at the methylene carbons 3 and 4.

Compound **2** rearranges almost irreversibly to **3**[8]



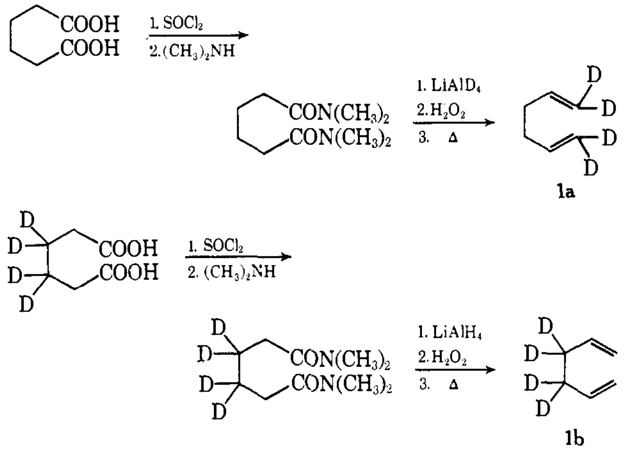
2 3

and by labeling positions 4 or 6 with deuterium it became possible to measure the corresponding isotope effects.

Methods and Results

The required biallyl-1,1,6,6-d_4 (**1a**) was prepared from adipic acid by the route shown in Scheme I.

Scheme I



Biallyl-3,3,4,4-d_4 (**1b**) was synthesized analogously starting from adipic-3,3,4,4-d_4 acid.

The synthesis of deuterated dicyanohexadienes **2a** and **2b** is outlined in Scheme II.

The deuterium constant of all intermediates and the final products was better than 95% (by nmr).

Equilibrium Studies. Samples of **1a** and **1b** were sealed in ampoules in the presence of small amounts of diphenylamine and heated to the required tempera-

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[1] Faculty of Pharmacy and Biochemistry, University of Zagreb, Zagreb, Yugoslavia.

[2] For a recent review see E. R. Thornton, *Annu. Rev. Phys. Chem.*, 17, 349 (1966).

[3] V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, 90, 418 (1968).

[4] V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, 87, 1382, 1383 (1965).

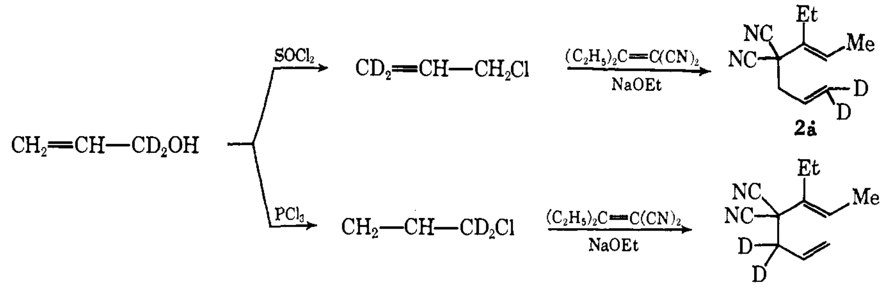
[5] For an excellent review of this subject, see E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 109 (1963).

[6] (a) T. Strelkov, Ph.D. Thesis, University of Zagreb, 1965; (b) K. Humski, Ph.D. Thesis, University of Zagreb, 1966; (c) R. Malojčić, K. Humski, S. Borčić, and D. E. Sunko, *Tetrahedron Lett.*, 2003 (1969); (d) K. Humski, T. Strelkov, S. Borčić, and D. E. Sunko, *Chem. Commun.*, 693 (1969).

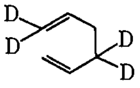
[7] S. J. Rhoads in "Molecular Rearrangements," P. De Mayo, Ed., Interscience, New York, N. Y., 1963, p 655.

[8] F. G. Foster, A. C. Cope, and F. Daniels, *J. Amer. Chem. Soc.*, 69, 1893 (1947).

Scheme II



ture. The progress of the reaction was followed by comparing the integrals of the nmr signals at τ 5.4–5.8 (terminal vinylic protons) and τ 8.3–8.6 (methylene protons). The final value of the ratio of integrals of these signals is equal to the equilibrium constant, *i.e.*, the thermodynamic deuterium isotope effect. From the rate at which the equilibrium was reached ($k_1 + k_{-1}$) and from the equilibrium constant (k_1/k_{-1}) the first-order rate constants for the conversion of **1a** to **1b**, k_1, and for the reverse process, k_{-1}, were calculated. The results are given in Table I. Each of the values in Table I is the result of a single determination.



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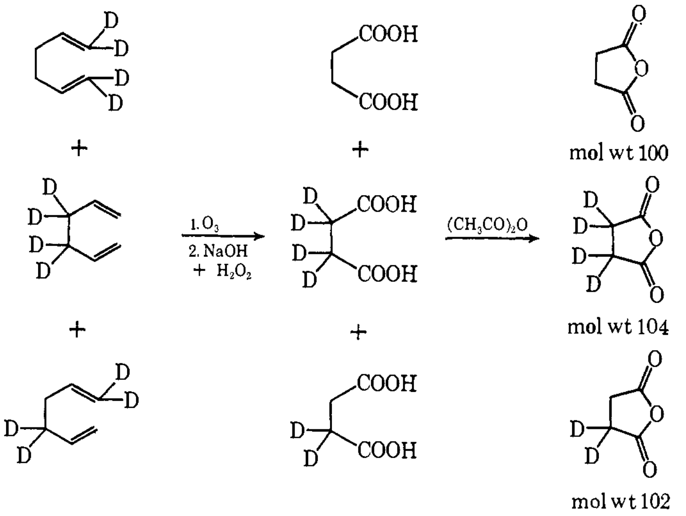
Crossover Reaction. The probability of an intra- and/or intermolecular crossover reaction *via* two allyl radicals which would result in the formation of **4** (in addition to the "normal" products **1a** and **1b**) is small. The homolytic thermal cleavage of biallyl is a path of considerably higher activation energy (E_a 46.5 kcal/mol[9]) than the Cope rearrangement (E_a 33 kcal/mol[9]). Moreover the E_a of 46.5 kcal/mol presupposes no limitations to geometries suitable for the Cope rearrangement. These limitations result in the loss of at least some of the stabilization of the allyl radicals. Experimentally, the presence of **4** in a mixture of **1a** and **1b** is not easily detected by nmr. Mass spectroscopic analysis of succinic anhydride obtained by degradation of the equilibrated mixture showed the absence of m/e 102 (see Scheme III).

Scheme III



For this rearrangement the $\Delta F°$ value ($\Delta F° = RT \ln K$) of 203 cal/mol was calculated. From this value the thermodynamic isotope effect of 10% per C–D bond was obtained at 25° assuming a zero entropy change.

Table I. Rates and Equilibrium Constants in the Thermal Rearrangement of Biallyl-d_4

Biallyl	Temp, °C	K [1b]/[1a]	$k_1 \times 10^7$, sec^{-1}	$k_{-1} \times 10^7$, sec^{-1}
1a	200	1.25		
1a	200	1.20		
1a	200	1.23	123	100
1a	150	1.27	1.88	1.48
1b	200	1.25		
	25	1.41 ± 0.02[a]		

[a] Calculated from data at higher temperatures. The uncertainty is standard error.

Kinetic Measurements. The rates of thermal rearrangement of compounds **2a**, **2b**, and undeuterated **2** into stable conjugated products were followed by measuring the increase in absorption at 238 nm. The calculated first-order rate constants are given in Table II. The energy and entropy of activation were determined by Cope[8] (E_a 25.8 kcal/mol and $\Delta S^{\ddagger}$ −11 eu).

Discussion

Since their discovery, secondary α-deuterium isotope effects have been rationalized in terms of vibrational changes accompanied with $sp^3 \rightarrow sp^2$ rehybridization at the reacting carbon.[10] Rather crude approxima-

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(9) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Harnstein, M. Jones, G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

(10) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 172.

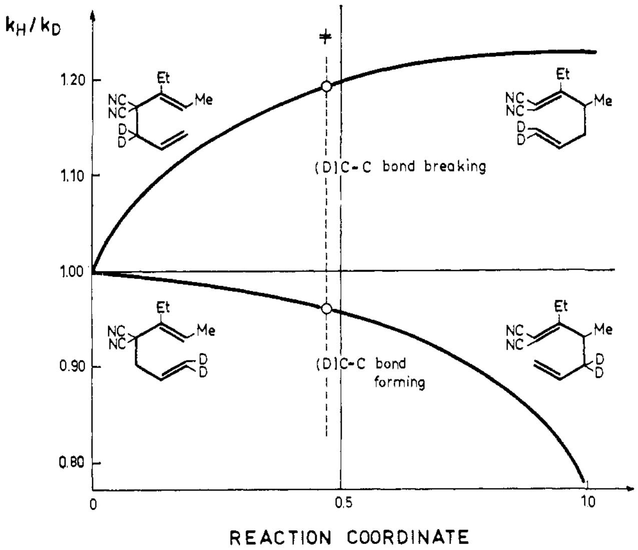

Figure 1. Possible correlation between the magnitude of isotope effects and the degree of bonding in the transition state.

tions yielded the value of k_H/k_D 1.40 as the maximum value of α effects.[11a] The usually observed, significantly lower value of 1.15–1.20 in solvolytic reactions has been explained [10,11] as being due to the proximity of the leaving group and possible solvation effects in the transition state. Only recently Shiner, *et al.*,[12] presented compelling experimental evidence that most differences in the magnitude of α effects are *de facto* caused by ground-state fractionation between substrates having different leaving groups. The actual bond order between the reacting carbon and the leaving group in the transition state seems to be only of secondary importance in most limiting solvolyses. It has been demonstrated[12] that in alkyl halides a change from chlorine to bromine results in a change of the α effect from 1.15 to 1.12 regardless of the nature of the alkyl group and that this is due to differences in the force constants in the reactants. The isotope effect on the equilibrium constant in the biallyl rearrangement represents a case where carbon is the leaving group (C–C bond cleavage) and where a complete $sp^3 \rightarrow sp^2$ rehybridization has taken place. The observed fractionation factor of 1.10 per deuterium for a change from a trigonal to a tetrahedral carbon gives a measure of the force constant changes associated with this kind of rehybridization.

Table II. First-Order Rate Constants and Secondary Deuterium Isotope Effects for Cope Rearrangement in *n*-Decane Solution

No. of expt	Compd	Temp,[a] °C	$k \times 10^4$ min^{-1}	k_H/k_D
1	**2**	90.0	5.43 ± 0.14[b]	1.23 ± 0.05
	2b		4.41 ± 0.14	
2	**2**	92.7	6.76 ± 0.13	1.15 ± 0.03
	2b		5.89 ± 0.11	
3	**2**	92.8	7.01 ± 0.06	0.94 ± 0.02
	2a		7.44 ± 0.09	
4	**2**		6.70 ± 0.08	
	2a	93.4	7.22 ± 0.07	0.93 ± 0.02
	2a		7.39 ± 0.06	0.91 ± 0.02
5	**2**		6.65 ± 0.06	
	2a	93.0	6.79 ± 0.05	0.98 ± 0.02
	2b		5.27 ± 0.13	1.26 ± 0.03
6	**2**		7.41 ± 0.06	
	2	93.9	7.28 ± 0.11	
	2b		6.31 ± 0.10	1.17 ± 0.02; 1.15 ± 0.02
			Av k_2/k_{2b}	1.19 ± 0.03
			Av k_2/k_{2a}	0.94 ± 0.02

[a] The temperature was measured in a constant temperature bath. The temperature in the cell was not accurately known because of experimental difficulties but was about 5° lower and constant to ±0.1°. [b] Uncertainties are standard errors.

The activation energy for the reaction **2** → **3** is 26 kcal/mol[8] while a reasonable estimate for ΔH is about -5 kcal/mol. This estimate is based on the nearly complete disappearance of the methyl group signal at τ 8.2 in **2** after heating for more than 10 half-lives at 110°. In Figure 1 the isotope effects are depicted as a function of the reaction coordinate. That is, the kinetic isotope effects must be strongly nonlinear functions of the position of the transition state on the reaction coordinate, because a transition state slightly less than 50% of the way from starting material to products produces an isotope effect as large as that on the equilibrium on the bond-breaking side while it produces only a small effect on the bond-making side. In the present case this qualitatively parallels the behavior of bond energies, because, in the breaking bond more than half the bond energy is lost, while, in the forming bond, less than half the bond energy has been gained. Based on the Urey–Bradly force field, changes in the nonbonded interactions of the type X–C–X were calculated as functions of the X···X distance.[13] A steep decrease of the force constant ensues with a relatively small increase of the X···X distance. From this model it can be confidently assumed that small elongations of the bond with the leaving group will result in a relatively high α effect whose magnitude will be only little affected by further increases in the C–X bond distance. The reverse has to be true for bond-forming processes (see Figure 1). However, the correlation between isotope effects and bond energy is not general. When α effects in direct displacement reactions[14] are compared with the effects obtained with a number of substrates prone to neighboring group participation,[15] the magnitude of the effects tends to center around two values. Direct nucleophilic displacements and aliphatic compounds with *n*-participating groups at a favorable position show effects close to unity, while π- and σ-participating systems regardless of the actual accelerations give rise to effects similar in magnitude to the ones observed in limiting solvolyses. Typical examples of such a behavior are shown below.

Since substrates with the same type of bond to the leaving group are compared, ground-state fractionation factors can be disregarded. This and other evidence led us to conclude that α effects are not a sensitive probe for bond cleavage or bond formation in the rate-deter-

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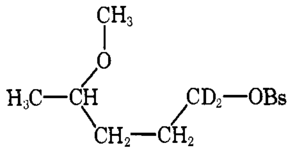
(11) (a) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, 80, 2326 (1958); (b) A. Streitwieser, Jr., C. L. Wilkens, and E. Kiehlmann, *ibid.*, 90, 1598 (1968).

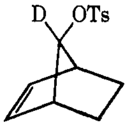
(12) V. J. Shiner, Jr., M. W. Rapp, E. A. Halevi, and M. Wolfsberg, *ibid.*, 90, 7171 (1968).

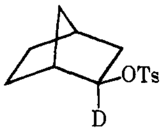
(13) (a) T. Shimanouchi, *Pure Appl. Chem.*, 7, 131 (1963); (b) J. B. Hendrickson, *J. Amer. Chem. Soc.*, 83, 4537 (1961).

(14) S. Seltzer and A. A. Zavitsas, *Can. J. Chem.*, 45, 2023 (1967).

(15) (a) R. Eliason, M. Tomić, S. Borčić, and D. E. Sunko, *Chem. Commun.*, 1490 (1968); (b) S. Borčić and D. E. Sunko, *Croat. Chem. Acta*, 33, 77 (1961).







k_H/k_D	1.01[15]	1.13[15]	1.20[17]
relative rates[16]	10^3	10^7–10^{11}	10^3

mining step. Another indication that this assumption is correct is found in the results obtained in acetolysis of cyclopropylcarbinyl benzenesulfonate.[15b] This reaction is accompanied by a competitive internal rearrangement to cyclobutyl benzenesulfonate which is unreactive under the experimental conditions. The α-deuterium isotope effects for acetolysis and internal rearrangement could therefore be measured and were found to be identical within the experimental error. This indicates that the whole α effect is obtained during the formation of the first and common intermediate to both reactions, the intimate ion pair. Further dissociation of the ion pair (or the return to cyclobutyl benzenesulfonate) proceeds without an isotope effect. This is in accord with the relation given in Figure 1. The relatively small C–X bond stretching necessary to produce an intimate ion pair will cause most of the α effect and further stretching will have little influence.

The alternative explanation of the experimental results is that the dissociation of the intimate ion pair and its return to rearranged benzenesulfonate proceed with exactly the same isotope effect, which is unlikely.

Since the Cope rearrangement is mechanistically similar to the Diels–Alder reaction and the Claisen rearrangement, it is pertinent to analyze some isotope effects observed in such reactions. Van Sickle[18] investigated the Diels–Alder reaction with deuterated substrates and observed for $sp^2 \rightarrow sp^3$ rehybridization small inverse effects (k_H/k_D 0.98–0.94/atom D) which were attributed to a small degree of bond formation in the transition state which resembles the reactants. Seltzer[19] studied the retro-Diels–Alder reaction ($sp^3 \rightarrow sp^2$ rehybridization) and also observed only "small" normal effects (k_H/k_D 1.08). For this reaction the author concluded that the geometry of the transition state still resembles the adduct, *i.e.*, the reactant. In our opinion accepting both explanations would represent a violation of the principle of microscopic reversibility. A similar argument can be found in McMichael's paper on the allylic rearrangement.[20] Here again observed discrepancies in the magnitude of α- and γ-isotope effects were ascribed to different degrees of bond formation and bond cleavage. Assuming a linear relationship between the isotope effect and bond order in a concerted reaction with a symmetrical transition state the equation $(k_H/k_D)_\alpha = (k_H/k_D)_\gamma$ should be obeyed, which is not the case. All these apparent discrepancies can be nicely explained by reference to Figure 1. However, at present, insufficient data are available for a more quantitative treatment.

Experimental Section

Adipic Acid Bis(N,N-dimethyl)amide.[21] An aqueous solution (211 g) containing 33% (1.55 mol) of dimethylamine was placed in a round-bottomed flask equipped with a stirrer and a dropping funnel. After the reaction mixture had been cooled with ice and salt, 57 g (0.312 mol) of adipoyl chloride[22] was added dropwise. The mixture was stirred overnight at room temperature and the water removed under vacuum. The residue was recrystallized from ether giving 51.7 g (83%) of the amide, mp 82°.

1,6-Bisdimethylaminohexane-1,1,6,6-*d*$_4$.[23] In a 500-ml flask 4 g (0.095 mol) of lithium aluminum deuteride was suspended in ether (300 ml) and the flask was attached to a Soxhlet extractor. In the thimble was placed 12.2 g (0.061 mol) of adipic acid bis(N,N-dimethyl)amide. After extracting for 60 hr, 4 ml of water, 4 ml of 15% sodium hydroxide, and 12 ml of water were carefully added. After the usual work-up the oily residue was dissolved in 10% hydrochloric acid. The acidic solution was washed with ether and then made basic with 10% sodium hydroxide until an organic layer appeared. After separation the water layer was extracted with ether, the combined organic layers were dried ($MgSO_4$), and the ether was removed under vacuum. Distillation of the residue gave 5.7 g (55%) of the diamine, bp 98° (12 mm).

1,5-Hexadiene-1,1,6,6-*d*$_4$ (1a).[22] 1,6-Bisdimethylaminohexane-1,1,6,6-*d*$_4$ (5.7 g, 0.33 mol) was placed in a 100-ml round-bottomed flask. The flask was cooled with ice and 25 ml of 30% hydrogen peroxide was added dropwise. The mixture was stirred overnight at room temperature. The end of the reaction was detected by negative phenolphthaleine test. Excess peroxide was destroyed by a catalytic amount of lead oxide. Water was evaporated *in vacuo*, and the residue was pyrolyzed *in vacuo* in an oil bath at 170°. The products were trapped in U-shaped tubes cooled with an acetone–Dry Ice mixture and liquid air. The condensate was separated from water, washed with 5% hydrochloric acid and saturated sodium carbonate solution giving 1.4 g (52%) of **1a**. The nmr showed almost no signals at τ 5.4–5.8, which would be due to four protons at positions 1 and 6. The multiplet at τ 4.5–5.0 (2 H) arises from protons at positions 2 and 5 and the multiplet at τ 8.3–8.6 (4 H) from protons positioned on carbons 3 and 4. Integration indicated 98% deuteration at positions 1 and 6.

Dimethyl Acetylenedicarboxylate.[24] Dicarboxylate was obtained from salt of acetylenedicarboxylic acid in 62% yield.[24]

Dimethyl Succinate-2,2,3,3-*d*$_4$. Dimethyl acetylenecarboxylate (58.2 g, 0.396 mol) was placed in a flask together with 580 mg of platinum oxide and stirred with a magnetic stirrer while deuterium gas was introduced (at atmospheric pressure). When the gas absorption ceased the product was filtered from the catalyst and distilled giving 58.0 g (94%) of ester, bp 96° (20 mm). The ester was more than 96% deuterated at positions 2 and 3 according to the nmr analysis.

1,4-Butanediol-2,2,3,3-*d*$_4$.[25] In 400 ml of tetrahydrofuran, 16.7 g (0.44 mol) of lithium aluminum hydride was dissolved and 58.0 g (0.387 mol) of dimethyl succinate-2,2,3,3-*d*$_4$ in 200 ml of THF was added dropwise to the stirred solution. Stirring and refluxing was continued for 6 hr. After working up in the usual way[25] the product was distilled giving 28.1 g (75%) of diol, bp 138° (11 mm).

1,4-Dichlorobutane-2,2,3,3-*d*$_4$.[26] To a stirred solution of 31.7 g (0.338 mol) of the diol and 4 ml of pyridine, 146 g (1.23 mol) of thionyl chloride was added dropwise. The stirring was continued

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(16) Rate accelerations relative to the structurally most similar derivative which cannot solvolyze with neighboring group participation.

(17) It has been claimed (C. C. Lee and E. W. C. Wong, *J. Amer. Chem. Soc.*, **86**, 2752 (1964)) that the isotope effect for the acetolysis of the *exo*-brosylate is 1.10 at 20°. We have repeated this experiment and found that the value reported by Lee arises from deuterium scrambling due to internal return (J. M. Jerkunica, Ph.D. Thesis, University of Zagreb, 1969).

(18) (a) D. E. Van Sickle, *Tetrahedron Lett.*, 687 (1961); (b) D. E. Van Sickle and J. O. Rodin, *J. Amer. Chem. Soc.*, **86**, 3091 (1964).

(19) (a) S. Seltzer, *ibid.*, **83**, 1861 (1961); (b) S. Seltzer, *ibid.*, **87**, 1534 (1965).

(20) K. D. McMichael, *ibid.*, **89**, 2943 (1967).

(21) F. Wild, "Characterization of Organic Compounds," University Press, Cambridge, 1947, p 181.

(22) E. Vogel, K.-H. Ott, and K. Gajek, *Justus Liebigs. Ann. Chem.*, **644**, 172 (1961).

(23) V. M. Mićović and M. Lj. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953).

(24) N. Rabjohn, Ed., "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 127.

(25) V. M. Mićović and M. Lj. Mihailović, "Lithium Aluminum Hydride in Organic Chemistry," Serbian Academy of Sciences, Beograd, 1955, p 34.

(26) R. Ahmad, F. Bumpus, and R. Strong, *J. Amer. Chem. Soc.*, **70**, 3392 (1947).

overnight, and then the mixture was refluxed for 3 hr. Ice was added to the cooled solution to destroy the excess of thionyl chloride and the organic layer was separated and washed successively two times with concentrated sulfuric acid, 15% sodium carbonate and water. The residue was distilled, giving 30.4 g (70%) of dichloride, bp 100° (150 mm).

Adiponitrile-3,3,4,4-d_4.[27] In a round-bottomed flask 19.5 g (0.4 mol) of sodium cyanide was dissolved by refluxing with 28 ml of water. 1,4-Dichlorobutane-2,2,3,3-d_4, 30.4 g (0.232 mol), was dissolved in 94 ml of 95% ethanol and added dropwise to the cyanide solution. The reaction mixture was refluxed for 35 hr. The solvent was removed under vacuum and the residue was extracted with 250 ml of ethyl acetate. The organic layer was dried and distilled *in vacuo* yielding 18.7 g (75%) of dinitrile, bp 178° (12 mm).

Adipic Acid-3,3,4,4-d_4.[28] Dinitrile (18.7 g, 0.173 mol) was mixed with 79.5 ml of concentrated HCl and heated under reflux for 4 hr. The solvent was removed under vacuum and the residue recrystallized from 100 ml of water, yielding 8 g (32%) of product, mp 151°.

1,5-Hexadiene-3,3,4,4-d_4 (1b).[21] Compound **1b** was prepared from adipic acid-3,3,4,4-d_4 by the same series of reactions as described for the preparation of **1a**. The yield was 1.5 g. Nmr showed almost complete absence of the protons in positions 3 and 4. Integration indicated that the deuteration was 97% complete.

Succinic Acid-d_4 (d_0).[29] Biallyl (1.4 g, 0.0171 mol), previously heated at 200° for 15 hr in a sealed ampoule, was diluted with 7 ml of methylene chloride. Ozone was bubbled through the solution for 5.5 hr. The ozonized solution was added dropwise to a stirred solution of 180 ml of 10% sodium hydroxide and 45 ml of 30% hydrogen peroxide. After 1 hr of stirring the methylene chloride was distilled off and stirring was continued overnight. Then the solution was made acidic with concentrated hydrogen chloride, saturated with sodium chloride, and continuously extracted with ether for 24 hr. Ether was distilled off and the residue crystallized from water, giving 0.2 g (0.002 mol) of succinic acid, mp 185°.

Succinic Anhydride-d_0 (d_4). Succinic acid (0.2 g, 0.002 mol) was placed in a 5-ml flask together with 0.5 g (0.005 mol) of acetic acid anhydride. The mixture was heated under reflux for 15 min. After cooling overnight in a refrigerator the precipitated anhydride was filtered off and dried; yield 0.1 g (50%), mp 119–121°

Allyl-1,1-d_2 Alcohol. This alcohol was prepared as described earlier.[30] The product was at least 97% deuterated in position 1 according to nmr.

Allyl-3,3-d_2 Chloride. The deuterated chloride was prepared by a modified procedure of Young, *et al.*[31] In a 100-ml three-necked flask equipped with magnetic stirrer, dropping funnel, and nitrogen inlet with a valve, two condensers were placed in a series. Between the two condensers a take-off adapter was inserted. The second condenser was connected with a vacuum line through two traps cooled to −80 and −180°, respectively. The apparatus was evacuated to 0.1-mm Hg and then filled with nitrogen. Pure thionyl chloride (50 ml) was added and cooled externally with a Dry Ice–acetone mixture. The system was evacuated to 80 mm and 5.0 g (83 mmol) of allyl alcohol was added dropwise in 50 min. Hydrogen chloride was condensed in the first trap. Then, the pressure was raised to 400 mm by introducing more nitrogen and the reaction mixture was stirred without cooling for an additional 30 min until it reached room temperature. Last traces of hydrogen chloride were removed by repeatedly evacuating the system to 40 mm and flushing with nitrogen. The obtained chlorosulfinic ester was decomposed by heating to 60–70° under 700 mm of nitrogen (cooling the condensers to −5° with methanol). Sulfur dioxide gas was captured in the trap cooled at −80°. After 2 hr of heating the temperature of the first condenser was raised to 45° while the second was kept at −5°. In this way most of the chloride and some thionyl chloride were removed. The product so obtained was purified by glpc using a 6-m silicone column at 60°. After flash distillation *in vacuo* at 10^{-2} mm, 1.67 g (25.5%) of pure product was obtained. The nmr spectrum integral indicated on the average 0.14 proton in the γ position (τ 5.0–5.3).

3,3-Dicyano-2-ethyl-1-methyl-1,5-hexadiene-6,6-d_2 (2a). Compound **2a** was prepared as described by Cope[32] using 420 mg (5.35 mmol) of allyl-3,3-d_2-chloride. The oily product was distilled *in vacuo* (10^{-5}) at room temperature and further purified by chromatography through the neutral alox III using petroleum ether (bp 35–40°) as an eluent. After one more distillation *in vacuo*, 160 mg (37.5%) of **2a** was obtained. The nmr spectrum integral indicated 0.13 proton in position 6 (τ 7.7–6.9) and 1.93 in position 4 (τ 7.3).

Allyl-1,1-d_2 Chloride.[33] From 2.6 g (33 mmol) of alcohol and 1.3 ml of phosphorus trichloride in the presence of 1 ml of pyridine, 2.1 g (72%) of chloride, bp 45°, was obtained. The nmr spectrum showed an absence of the vinyl protons doublet at τ 4.32.

3,3-Dicyano-2-ethyl-1-methyl-1,5-hexadiene-4,4-d_2 (2b).[32] Compound **2b** was prepared in the same manner as **2a** using allyl-1,1-d_2 chloride. The nmr spectrum showed almost complete absence of the methylene protons doublet at τ 7.3.

3,3-Dicyano-2-ethyl-1-methyl-1,5-hexadiene (2).[32] The synthesis of **2** was performed in the same way as for **2a** using unlabeled allyl chloride. Nmr spectrum showed a triplet due to methyl protons from the ethyl group at τ 8.8 (3 H), a doublet of a methyl group at τ 8.2 (3 H), a quadruplet from the methylene in the ethyl group from τ 7.5 to 8.0 (2 H), a doublet of methylene at τ 7.3 (2 H), and an unresolved envelope of protons attached to double bonds from τ 7.7 to 6.9 (4 H).

Equilibrium Constant Measurement. Traces of diphenylamine were placed in a glass tube 6 mm in diameter together with about 0.25 ml of biallyl. The tube was evacuated three times on the vacuum line and sealed. After heating for definite time periods (see Table I) a sample was distilled *in vacuo* into nmr tubes and the composition of the mixture was determined.

Kinetic Measurements. The rates of rearrangement of **2**, **2a**, and **2b** were measured directly at 238 nm in the cell of a Beckman DU G-2400 spectrometer. The cell compartment was previously stabilized at the corresponding temperature for at least 6 hr. Additional temperature equilibrium was allowed after inserting the samples and before the first readings were taken. The instrument was not equipped with a temperature recorder and the correct temperature in the cell was unknown. With the crude approximation the temperature in the cell was approximately lower by 5° than that of the constant temperature bath. Care was taken to randomize the order in which the readings were taken from the various reaction mixtures in order to minimize the errors.

The concentration of samples was *ca.* 0.1 mg/10 ml of *n*-decane. Sample cells (1 cm) were used with an approximate volume of 2.5 ml. *n*-Decane was chosen as solvent because of the high boiling point (164°) and low volatility. Only rate constants calculated from simultaneous measurements could be compared. Rate constants were obtained using the usual integrated form of the first order rate law. Data were accumulated from 20–75% completion. The rate constant and infinite-time absorbance were calculated using a weighted least-squares criterion of fit.

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[27] H. Gilman and A. H. Blatt, Ed., "Organic Syntheses," Coll. Vol. I, Wiley, New York, N. Y., 1947, p 536.

[28] H. Gilman and H. Blatt, Ed., "Organic Syntheses," Coll. Vol. I, Wiley, New York, N. Y., 1947, p 189.

[29] T. Strelkov, S. Borčić, and D. E. Sunko, *Croat. Chem. Acta*, 34, 243 (1962).

[30] P. D. Bartlett and F. A. Tate, *J. Amer. Chem. Soc.*, 75, 91 (1955).

[31] S. H. Sharman, F. F. Caserio, R. F. Nystrom, Y. C. Leak, and W. G. Young, *ibid.*, 80, 5965 (1958).

[32] A. C. Cope, K. E. Hoyle, and D. Heyl, *ibid.*, 63, 1843 (1941).

[33] R. F. Nystrom, personal communication.