

Stereochemistry and Secondary Deuterium Kinetic Isotope Effects in the Cycloadditions of Diphenylketene with Styrene and Deuteriostyrenes¹

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Abstract: The concerted (2 + 2) cycloaddition between styrene and diphenylketene is highly stereoselective: *cis*- β -deuteriostyrene leads to the 2,2,3-triphenyl-4-deuteriocyclobutanone having cyclobutyl hydrogens in a *cis* relationship. Secondary deuterium kinetic isotope effects for the reaction are (k_H/k_D) = 0.91 at the β position and (k_H/k_D) = 1.23 at the α position of styrene at 65°.

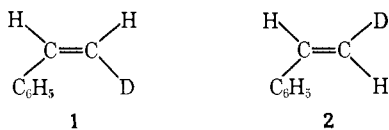
Diphenylketene adds to styrene to form the adduct 2,2,3-triphenylcyclobutanone.⁴ Through comparing the rates of analogous cycloadditions of diphenylketene with substituted styrenes and with 1,1-diarylethylenes, the process was recognized to be a one-step addition: no intermediate species such as a dipolar ion or diradical corresponding to a local energy minimum intervenes between reactants and product.⁵ The meager solvent effects on reaction rate also supported this conclusion.⁵

Two additional mechanistic criteria for the one-step or two-step nature of the diphenylketene-styrene cycloaddition were employed in the present study. The stereochemistry and the secondary deuterium isotope effects of the reaction were established.

Results

Stereochemistry. A desire to introduce the needed asymmetry with a minimum perturbation of the styrene molecule dictated selection of *cis*- or *trans*- β -deuteriostyrene as substrate.

Phenyldeuterioacetylene, prepared by treating phenylacetylene with a suspension of calcium oxide in deuterium oxide, was hydroborated with bis(3-methyl-2-butyl)borane⁶ at 0° and the product was decomposed with acetic acid. The *cis*- β -deuteriostyrene (**1**) obtained was 95–96% isotopically and stereochemically pure.



Earlier attempts to prepare **1** or **2** through deuteriolysis of the Grignard reagents derived from *cis*- and *trans*- β -

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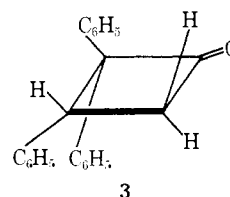
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bromostyrene,^{7,8} reduction of phenyldeuterioacetylene with hydrogen over Lindlar catalyst,⁹ and treatment of phenyldeuterioacetylene with a freshly prepared chromous sulfate solution^{10,11} all led to β -deuteriostyrene of insufficient stereochemical purity.

To determine the stereochemistry of the cycloadduct from diphenylketene and *cis*- β -deuteriostyrene by nmr, it was first necessary to analyze the spectrum of the undeuterated adduct **3**. Although the chemical shifts of the protons may change slightly on nearby deuterium substitution, the coupling constants will remain invariant.¹² The nmr spectrum of cyclobutanone **3** in deuteriochloroform appeared as a triplet centered at τ 5.68 (relative to TMS), 1 proton, and a doublet at 6.72 ppm (2 H), skewed in the direction of the triplet.



This spectrum was suggestive of an ABX or ABK system in which the chemical shifts of protons A and B are nearly identical, a conclusion supported by the broad line width of the doublet. Adducts prepared from a number of substituted styrenes, including 2,6-dimethylstyrene, did not exhibit any greater separation of the AB protons. But in bromobenzene or DMSO-*d*₆ the center peak of the triplet and the high field peak of the doublet each showed splitting into two peaks. On a first-order basis,¹³ splitting constants of $J_{AB} \sim 0$ Hz, $J_{AC} = 8.4$ Hz, and $J_{BC} =$

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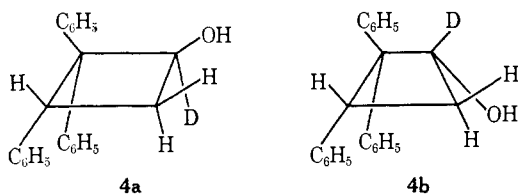
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9.5 Hz are obtained. These are clearly incompatible with the Karplus calculations¹⁴ which would predict $J_{AB} \approx -24$ Hz ($H_A C H_B$ angle $\approx 110^\circ$) and with recently observed negative geminal couplings of roughly half that magnitude in cyclobutyl compounds.¹⁵ The system resembles closely the "deceptively simple" ABX system¹⁶ where $\delta_{AB} \rightarrow 0$ and $(J_{AX} - J_{BX})/2J_{AB} \rightarrow 0$. Attempts to analyze the system as either an ABC or ABK spectrum according to the procedure of Garbisch¹⁷ led only to inconsistent results. Irradiation at the center of the triplet did not simplify the spectrum.

In the limiting ABC case, where $\delta_{AB} = 0$, the spectrum becomes that of an AB_2 system. Analysis of the spectrum of **3** as an AB_2 system¹³ gave $J_{AB} = -11.7$ Hz. That **3** was indeed best represented as an AB_2 system was confirmed by the nmr spectrum of the adduct prepared from α -deuteriostyrene and diphenylketene, which showed a single unsplit non-aromatic absorption at τ 6.75 ppm.

The most obvious means of distinguishing the two methylene protons in **3** would be to introduce additional asymmetry into the molecule at the carbonyl carbon. Reduction of the ketone with lithium aluminum deuteride in ether gave an excellent yield of a single secondary alcohol; both thin layer chromatography and the nmr spectrum indicated the presence of but a single isomer (**4a** or **4b**).



If a chloroform solution of the cyclobutanol is shaken briefly with deuterium oxide, the nmr absorption due to OH is lost; the other upfield absorptions from the three aliphatic protons can be analyzed as an ABC system.¹⁸ The least squares best-fit parameters to the 100-MHz spectrum of the alcohol are, for the chemical shifts, 84.2 (H^1), 60.2 (H^2), and 185.6 (H^3) (with respect to an arbitrary reference point; see Experimental Section for τ values) and for the coupling constants, $J_{12} = -11.06$, $J_{13} = 8.31$, and $J_{23} = 11.2$ Hz. The average deviation between the twelve observed and calculated transition frequencies was 0.16 Hz.

Correlations of experimentally observed vicinal coupling constants in cyclobutanes with expectations based on valence bond¹⁹ or antisymmetrized molecular orbital²⁰ calculations have not been entirely satisfactory,^{21,22} in part because of conformational ambiguities in the cyclobutanes used to test theory. For a dihedral

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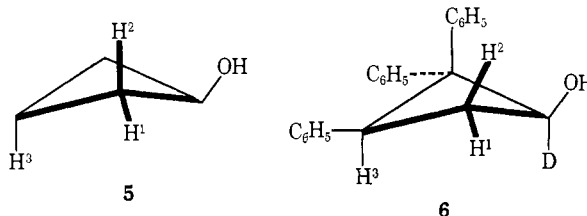
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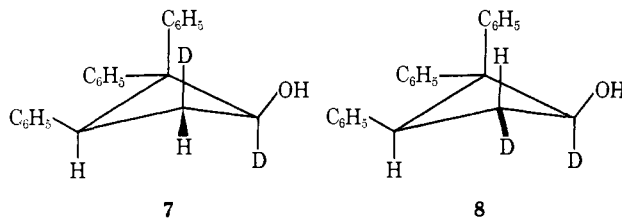
angle between 155 and 180° (*trans*, axial-axial), the Conroy curve gives J_{HH} as 10–11 Hz. Observations for several nonplanar cyclobutanes are consistent with this prediction,^{23,24} and accordingly the 11.2-Hz coupling constant in **4** may be assigned to the *trans* protons. The *cis* coupling is then 8.31 Hz. The same trend has been observed by Wiberg and Barth for the unsubstituted cyclobutanol (**5**): $J_{13} = 7.9$ Hz, and $J_{23} = 10.4$ Hz.¹⁵ The stereochemistry at C(1) may be assigned, placing the hydroxyl group equatorial and *trans* to the adjacent, most downfield and equatorial methylene proton, thus completely defining the system (**6**).



The difference in chemical shift between methylene protons 1 and 2 in the alcohol **6** is somewhat smaller than in the parent system **5** (0.24 vs. 0.32 ppm, equatorial protons at lower field), presumably because H^2 in **6** is deshielded by proximate phenyl groups more than H^1 .²⁵ The stereochemical outcome of the reduction might have been anticipated from previous experience.²⁶

Diphenylketene and *cis*- β -deuteriostyrene (95–96% d_1) gave a cycloadduct which was reduced with lithium aluminum deuteride. The nmr spectrum of the resulting alcohol in $CDCl_3$ at 100 MHz contained two doublets coupled to each other by 8.25 ± 0.20 Hz and separated by 104 ± 3 Hz. The only other absorptions visible were due to a small amount of the undeuterated material. Thus the alcohol may be assigned structure **7** and the addition of diphenylketene to styrene proceeds stereospecifically and *cis* with respect to the olefin. A nmr spectrum of a synthetic mixture of the *cis* (**7**) and *trans* (**8**) alcohols, prepared from a mixture of *cis*- and *trans*- β -deuteriostyrene, indicated that a minimum of about 4% of the *trans* alcohol could have been detected in the presence of the *cis* alcohol.

Figure 1 shows the observed nmr spectra for the nonaromatic protons of cyclobutanols **6** and **7**.



Secondary Deuterium Kinetic Isotope Effects. A study of competitive reactions between styrene and α -deuterio- or β , β -dideuteriostyrene with diphenylketene was conducted to secure the corresponding sec-

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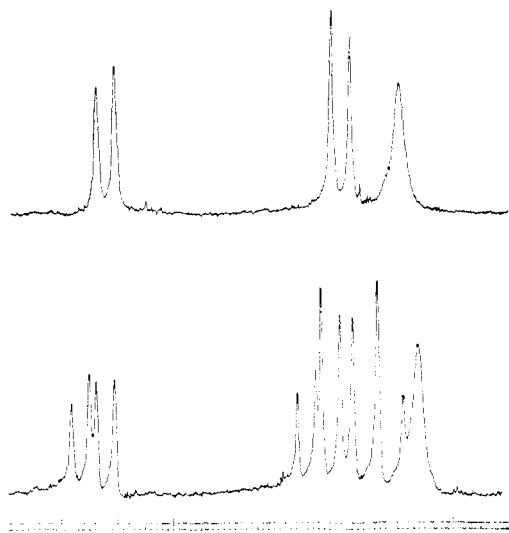


Figure 1. Observed nmr spectra at 100 MHz for the aliphatic protons of cyclobutanols **6** (below) and **7** in deuteriochloroform. The chemical shift of the broad hydroxy proton absorption upfield was concentration dependent. See text for chemical shift and coupling constant data.

ondary deuterium kinetic isotope effects.²⁷ The two deuterated styrenes were prepared through the correspondingly labeled 1-phenylethanol. Acetophenone-*d*₃ from the base-catalyzed exchange of acetophenone in D₂O was reduced with lithium aluminum hydride, and the secondary alcohol was dehydrated in the presence of a trace of iodine to give β,β -dideuteriostyrene, 97–98% isotopically pure according to 100-MHz nmr analysis. Acetophenone and lithium aluminum deuteride, in the same scheme, gave α -deuteriostyrene, 99+ % isotopically pure. Both labeled styrenes were contaminated by trace amounts ($\leq 4\%$) of deuterated ethylbenzene.

The intermolecular competition reactions were run with diphenylketene and an excess of an approximately 1:1 mixture of deuterated and undeuterated styrene. The reaction mixture was sealed under nitrogen in base-washed glass tubes and placed in a bath at $65 \pm 0.1^\circ$. Polymerization of the styrene under these conditions was relatively slow. In those runs with low styrene to ketene ratios, no polymer could be detected; in runs with higher styrene concentrations, some polymeric material was found, but a large excess of styrene was always present at the end of the reaction.

It is easily shown²⁸ that when the styrene is in large excess or the extent of reaction is small that the ratio of rate constants is given by eq 1, where S stands for styrene and P for the cycloaddition product. The

$$(k_H/k_D) = (S_D/S_H)(P_H/P_D) \quad (1)$$

correction of the rate constant of a *d_n* species to a per deuterium basis is given by expression 2.

$$(k_H/k_D)_{d_1} = (k_H/k_D)_{d_n}^{1/n} \quad (2)$$

In the case of β,β -dideuteriostyrene correction was also made for the very small *d*₁ content. If the conditions for eq 1 do not hold in the experimental situation, a

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trend toward a larger isotope effect should be noted as the relative excess of styrene increases. No such trend is noted for the reactions of α -deuteriostyrene; a slight trend is observed in the reactions of β,β -dideuteriostyrene. In either case, such a condition would mean that the actual isotope effects might be larger than observed.

The results, calculated on a per deuterium basis, are given in Table I. The kinetic isotope effect k_H/k_D

Table I. Secondary Deuterium Isotope Effects in (2 + 2) Cycloadditions between Diphenylketene and Deuteriostyrenes at 65°

Sample	Run	Molar ratio styrene/ketene	k_H/k_D	
			Mass spectrum	100 MHz nmr
$H_5C_6CD=CH_2$	1	1.70	1.213	1.254
	2	2.86	1.234	1.221
	3	4.01	1.250	<i>a</i>
	4	4.37	1.231	1.208
		Av	1.235	1.227
$H_5C_6CH=CHD^b$	5	1.59	0.920	0.936
	6	2.34	0.913	0.899
	7	2.95	0.904	0.903
	8	4.50	0.896	0.902
		Av	0.908	0.910

^a Insufficient sample for nmr spectrum. ^b Reaction run with β,β -dideuteriostyrene, and k_H/k_D calculated on per deuterium basis.

at the β position of styrene at 65° is 0.91, while k_H/k_D for substitution at the α position is 1.23.

The (2 + 2) cycloadditions of dimethylketene to *cis*- and *trans*-1-butenyl ethyl ether,²⁹ of diphenylketene to *cis*- and *trans*-1-propenyl propyl ether,^{30,31} and of dichloroketene (generated *in situ*) to *cis*- and *trans*-cyclooctene³² occur stereoselectively; the geometrical relationships in the starting olefins are retained in the cycloadducts, just as they are in the styrene-diphenylketene addition. Such stereospecificity is consistent with, but does not require, formulation of the reaction as a concerted process in which no short-lived intermediate lies between addends and cycloadduct along the reaction coordinate.

The secondary deuterium kinetic isotope effects³³ observed for the styrene-diphenylketene reaction seem to require a concerted mechanism.

Streitwieser and coworkers predicted on theoretical grounds that a change from sp² to sp³ hybridization at an isotopically substituted carbon atom between ground state and transition state would give rise to an inverse secondary deuterium isotope effect, $k_H/k_D < 1$.³⁴ This calculated isotope effect was linked to a

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change in C–H vibration frequencies and was consistent with observations in solvolysis reactions. More recently applications of these principles have been made to the study of Diels–Alder reactions^{35,36} and radical additions.³⁷ In general the isotope effects are small (1–10%) and inverse, in harmony with prediction for the sp^2 to sp^3 hybridization change. For the Diels–Alder reactions, the low magnitude of the effect has been taken to indicate that the transition state in the reaction resembles the reacting species.^{36b} Competitive experiments between dienophiles isotopically substituted at either terminus of the π system result in product ratios of 1.0 or close to this value, supporting a transition state in which bond making is nearly the same at both centers.^{36c} In radical additions at olefinic centers, the carbon becoming the new radical center shows no secondary deuterium isotope effect;³⁷ it retains a nominal sp^2 hybridization throughout the addition.

One might anticipate, then, that a one-step (2 + 2) cycloaddition would be characterized by inverse secondary deuterium isotope effects at each terminus of an olefinic reactant; the inequality of the two inverse isotope effects would provide a measure of the asymmetry in the transition state. A two-step mechanism would give an inverse kinetic isotope effect at the center first bonded to the other reactant and no effect at the adjacent carbon. Thus the distinction between an asymmetric one-step and authentic two-step mechanism would depend on accurate determinations of both kinetic isotope effects and, possibly, on a value judgment between “small” and negligible deviations below 1.0 of k_H/k_D .

The study of the addition of diphenylketene to 1-deuteriocyclohexene by Katz and Dessau³⁸ indicated that the transition state was unsymmetrical, but no separation of the observed product ratio into the two contributing isotope effects, and no conclusions as to the number of steps in the overall process, were possible.

The observed $k_H/k_D = 0.91$ at the β position of styrene is in complete accord with expectation: at the rate-determining transition state, the hybridization of the β carbon has progressed from sp^2 toward sp^3 as the new bond between that carbon and the carbonyl carbon of diphenylketene increases in strength. The effect at the α position, $k_H/k_D = 1.23$, agrees neither with the result anticipated from the simplest concerted model, wherein both olefinic carbons of styrene form new parallel bonds simultaneously ($k_H/k_D < 1$), nor with the prediction based on the diradical, two-step model ($k_H/k_D = 1.0$). The observed “normal” secondary deuterium isotope effect is not explicable in terms of conventional models: the standard array

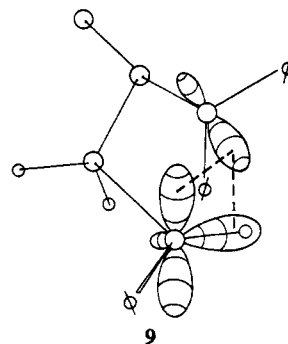
of steric, hyperconjugative, inductive, and hybridization effects all seem unable to serve as basis for rationalizing the experimental result.

A substantial normal deuterium isotope effect has become associated with the twisting of an sp^2 carbon out of conjugation with an adjacent p orbital as a necessary prelude to bonding with another atom. Such normal isotope effects have usually been observed or interpreted as intramolecular secondary deuterium effects on a product-determining rather than a rate-determining portion of a reaction profile.^{36f,39} They have been attributed to a faster rate of rotation about a protiomethylene–carbon than about a deuteriomethylene–carbon bond. Presumably the difference in the moments of inertia between a CD_2 and CH_2 group makes an important contribution to the isotope effect.

For the diphenylketene–styrene addition such an interpretation of the effect is less convincing; no large difference in moment of inertia distinguishes H_5C_6CH from H_5C_6CD .

A model which we currently favor, and suggest as a useful approach toward explaining the large normal isotope effect at the α position of styrene, regards the C_α –H bond as being considerably weakened in the transition state through interaction of this bond with the approaching p orbital.

The addition of diphenylketene to styrene can be considered formally as a (2 + 2 + 2), *sss* cycloaddition in which the ketene employs two orbitals originally having a 90° rather than a 180° dihedral angle for forming the new bonds. The orbital symmetry prohibition against a concerted thermal *cis,cis* (*ss*) addition between an olefin and two parallel p orbitals on the C=C bond of the ketene leads to a hypothetical geometry for the activated complex in which the p orbitals of the second, less electrophilic carbon of diphenylketene and C_α of styrene are not well disposed for profitable overlap (9). The system is lowered in energy through interaction between the apposite C_α –H bond of styrene and p orbital of diphenylketene.



This model might be taken as a variant of a more common effect contributing to isotope effects: hyperconjugation. A C–H bond geometrically well positioned to overlap with a p orbital can do so more effectively than the corresponding C–D bond.^{33,34,40} In the present system, the p orbital interacting strongly with the C_α –H bond happens to have been originally associated with the other addend.

The (2 + 2) cycloaddition of dimethyl azodicarboxylate with ethyl vinyl ether and deuterated analogs

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(38) T. J. Katz and R. Dessau, *ibid.*, **85**, 2172 (1963).

occurs with secondary deuterium isotope effects similar to those observed for the diphenylketene-styrene reaction: for $\text{H}_2\text{C}=\text{vs. HDC}=\text{}$, $k_{\text{H}}/k_{\text{D}}=0.83$, while the $=\text{CH}-, =\text{CD}-$ competition gave $k_{\text{H}}/k_{\text{D}}=1.12$ at an unspecified temperature.⁴¹ These results were interpreted⁴¹ in terms of hybridization change from sp^2 to sp^3 at $\text{H}_2\text{C}=\text{}$ between ground and transition states; the unexpected "normal" $k_{\text{H}}/k_{\text{D}}=1.12$ was not explained and the addition was considered a two-step reaction.

The observed $k_{\text{H}}/k_{\text{D}}=1.12$ is as inconsistent with a two-step process wherein the $=\text{CH}-$ carbon becomes a radical center in the intermediate as it is with an sp^2 to sp^3 hybridization change. Concertedness has not been identified previously with "simultaneous change of hybridization at all involved centers"⁴¹ in a cycloaddition. The concept has been linked with the absence of one or more intermediates separating reactants and products. When there is no intermediate in a cycloaddition, then "bonding is established simultaneously at more than one site,"⁴² necessarily. Nothing in this assertion, however, requires the bonding at the transition state to correspond precisely with the localized bond conceptualizations frequently employed for ground state molecules. At the more substituted olefinic carbon of styrene or ethyl vinyl ether the geometrical and orbital symmetry constraints lead to the establishment of bonding through a hyperconjugative interaction between orbitals originally associated with distinct reactants. Another rationale may soon outmode this purely qualitative interpretation of the normal isotope effect in such cycloadditions, but the basic conclusion seems secure. Something quite noticeable through isotope effects is happening at both carbon atoms in the transition states of these reactions; both are establishing bonding with atoms in their cycloaddition partners, though they accomplish this through dissimilar mechanisms.

That experimental criteria for identifying the one-step or two-step character of a cycloaddition may be used only in special cases,⁴³ and that theoretical rules⁴⁴ provide the only generally applicable test for concertedness or nonconcertedness,⁴⁵ seem too bleak and pessimistic conclusions for an experimental science. The theoretical appraisal of ketene-olefin cycloadditions has only recently⁴⁴ reversed an earlier conclusion that the reaction had to be a two-step process.⁴⁵ The utility of orbital symmetry cannot be denied, but neither this nor any other theory can substitute for an operational, experimentally determinable standard for concertedness.

Theory, as now formulated, permits the diphenylketene-styrene reaction to be a one-step reaction. Reaction kinetics, using substituted styrenes, solvent effects on rates, stereochemical specificity, and secondary deuterium isotope effects all point toward the concertedness of this cycloaddition. In the absence of any piece of experimental evidence adduceable as support for a

nonconcerted mechanism, one conclusion follows: the cycloaddition of diphenylketene with styrene is a concerted reaction.

Experimental Section

Melting points were obtained on a Kofler micro heating stage using a calibrated thermometer; boiling points are uncorrected. The microanalysis was done by Mr. J. Nemeth and his associates, Urbana, Ill. Mr. J. Wrona obtained the low resolution mass spectra with an Atlas CH-4 instrument. Nmr spectra were recorded on a Varian Associates Model HA-100 spectrometer with the collaboration of Mr. R. Thrift.

Diphenylketene⁹ was freshly redistilled at reduced pressure under a nitrogen atmosphere just prior to use.

2,2,3-Triphenylcyclobutanone and deuterated analogs were prepared through the thermal cycloadditions of diphenylketene with styrene or deuteriostyrenes.

1-Phenylethanol-1-*d* was prepared by the reduction of acetophenone (14.8 g, 123 mmol) with lithium aluminum deuteride.⁴⁶ Distillation gave 13.6 g (89%) of the C-deuterated alcohol, bp 51–54° (0.5 mm) [lit.⁴⁶ bp 79° (2.3 mm)], $n_{\text{D}}^{20} 1.5260$ (lit.⁴⁶ $n_{\text{D}}^{20} 1.5267$).

1-Phenylethanol-2-*d*₃. The reduction of 12.8 g (104 mmol) of acetophenone-*d*₃⁴⁷ and 1.31 g (35 mmol) of lithium aluminum hydride (35 mmol) led to 11.7 g (90%) of distilled 1-phenylethanol 2-*d*₃.

α -Deuteriostyrene. In a 50-ml round-bottomed flask equipped with a distillation head was placed 6.6 g (54 mmol) of 1-phenylethanol-1-*d*, 10 mg of iodine, and 10 mg of *p*-*t*-butylphenol as a polymerization inhibitor. A few milligrams of *sym*-trinitrobenzene was placed in the receiver, and the distillation flask was heated slowly in an oil bath to 260°. Steady distillation occurred as the bath temperature was raised from 130 to 240°. The distillate was shaken with ether; the organic layer was separated, washed with a 15% sodium thiosulfate solution and with water, dried over magnesium sulfate, and filtered. Distillation gave 1.96 g (56% based on recovered alcohol) of α -deuteriostyrene, bp 49–52° (25 mm), and 2.35 g of a red liquid which proved to be primarily unconverted alcohol. No signal due to α -protons⁴⁸ could be observed in the 100-MHz nmr spectrum of the olefin.

β,β -Dideuteriostyrene. The procedure described above for the preparation of α -deuteriostyrene was employed using 11.7 g (93.5 mmol) of 1-phenylethanol-2-*d*₃ and 20 mg of iodine. A second distillation gave 5.01 g (51%) of β,β -dideuteriostyrene, bp 49–55° (25 mm). The 100-MHz nmr spectrum indicated the styrene was 96–97% completely labeled, in accordance with the amount of undeuterated material in the acetophenone used to prepare the starting alcohol.

Secondary Deuterium Isotope Effects in the Addition of Diphenylketene to Deuterated Styrenes. An approximately 50:50 mol % mixture of styrene-*d*₀ and α -deuteriostyrene or β,β -dideuteriostyrene was prepared. Weighed amounts of freshly distilled diphenylketene and the styrene mixture (Table I) were sealed into 7.4-cm combustion tubes under nitrogen. The tubes had been previously washed, rinsed with acetone, and oven dried.

The sealed tubes were heated in a kinetic bath for 12 hr at 65.0 \pm 0.1°. The crude adducts, obtained in quantitative yields, were each recrystallized three times from petroleum ether (bp 60–68°) to give samples of mp 135–136°. The ratio of *d*₀ to *d*_{*n*} (*n* = 1 or 2) styrene used in the competition experiments was determined through analysis of the adduct obtained by treating an excess of diphenylketene with the styrene mixture, and from direct mass spectral analysis of the styrene samples.

Measuring *M* + 1 or *M* + 2 to *M* mass spectral peak ratios and correcting for contributions of the *d*₀ adduct (*m/e* 298) to the *m/e* 299 and 300 ion abundances, using factors determined from the mass spectrum of undeuterated adduct, gave (*P*_D/*P*_H) and (*S*_H/*S*_D) values required in eq 1. None of the spectra exhibited a measurable *M* – 1 peak.

Integrated relative intensities for methylene and methine protons of adducts in 100-MHz nmr spectra gave an independent measure of *d*₀ to *d*_{*n*} ratios in the styrene reactant and cyclobutanone adducts. The scatter from the mean of the multiple integrations for a single

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(45) Compare D. G. Farnum, J. R. Johnson, R. E. Hess, T. B. Marshall, and B. Webster, *J. Amer. Chem. Soc.*, 87, 5191 (1965).

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(47) We thank Dr. D. J. W. Goon for a generous gift of acetophenone-*d*₃.

(48) T. Yoshino, Y. Manabe, and Y. Kikuchi, *J. Amer. Chem. Soc.*, 86, 4670 (1964).

run compared to the scatter observed in the mass spectral analyses indicated that the latter method was more precise. The differences between the overall averages for the mass spectral and nmr data are, however, well within experimental accuracy: the results are summarized in Table I.

Phenylacetylene- d_1 . In a 100-ml round-bottomed flask equipped with stirring bar and reflux condenser was placed 22.0 g of phenylacetylene and a suspension of 3 g of calcium oxide in 20 ml of deuterium oxide. The material was stirred for 24 hr at 40°. The organic layer was decanted, the aqueous suspension was extracted with ether, the combined organic phases were dried over magnesium sulfate and filtered, and the ether was removed under vacuum. Analysis by nmr spectroscopy indicated that the material was 85% d_1 . The exchange was repeated and the phenylacetylene was distilled to give 20.4 g (93% recovery) of 97–98% d_1 material.

***cis*- β -Deuteriostyrene.** A 500-ml three-necked round-bottomed oven-dried flask was fitted with reflux condenser, addition funnel, magnetic stirring bar, nitrogen inlet, and thermometer. The flask was flushed with dry nitrogen and kept under a nitrogen atmosphere during the reaction. A mixture of 100 ml of dry tetrahydrofuran (distilled from lithium aluminum hydride), 37.4 g (0.535 mol) of 2-methyl-2-butene (Aldrich, distilled), and 6.82 g (0.180 mol) of sodium borohydride was placed in the flask and cooled to 0° in a Dry Ice–isopropyl alcohol bath. A mixture of 38.0 g (0.244 mol) of freshly distilled boron trifluoride etherate in 40 ml of tetrahydrofuran was added over a period of 1.5 hr while the reaction temperature was held at 0°. The mixture was stirred for 2 hr at 0°, and then 22.7 g (0.222 mol) of freshly distilled phenylacetylene- d_1 (97–98% deuterated) in 20 ml of tetrahydrofuran was added as rapidly as possible while keeping the temperature between 0 and 5°. The mixture was allowed to warm to room temperature and stirred for 1 additional hr; the excess hydride was decomposed with a few milliliters of ethylene glycol. After dropwise addition of 50 ml of glacial acetic acid, the mixture was stirred overnight and poured into 200 ml of ice water. The organic layer was separated, washed with aqueous sodium bicarbonate, dried over magnesium

sulfate, and distilled, employing a trace of Dow Antiform A and a 12 cm Vigreux column. The crude product was redistilled to give 5.9 g (26%) of *cis*- β -deuteriostyrene, bp 52–53° (30 mm), 95–96% isotropic purity by 100-MHz nmr.

2,2,3-Triphenylcyclobutanol. In a three-necked, round-bottomed flask equipped with magnetic stirring bar, reflux condenser with drying tube, and addition funnel was placed 0.10 g (2.6 mmol) of lithium aluminum hydride in 20 ml of anhydrous ether. A solution of 1.0 g (3.3 mmol) of 2,2,3-triphenylcyclobutanone in 100 ml of anhydrous ether was added dropwise to the stirred suspension. The mixture was heated under reflux with stirring for 20 hr and decomposed by the addition, in succession, of 0.1 ml of aqueous 10% sodium hydroxide and 0.3 ml of water. The solids were removed by filtration and washed with several portions of ether. The combined organic materials were dried over magnesium sulfate, filtered, and concentrated under vacuum. Three recrystallizations of the crude material (0.90 g, 90%) gave white crystals, mp 100–101°, from petroleum ether (bp 60–69°).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 88.16; H, 6.72.

The nmr spectrum of the alcohol exhibited absorptions at τ 2.4–3.2 (m, 15 H), 5.2 (d, 1 H), 6.05 (d of d, 1 H), 6.9–7.5 (m, 2 H), and 2.4 (broad s, 1 H). The absorption at τ 2.4 ppm disappeared when the deuteriochloroform solution of the adduct was shaken with deuterium oxide. The detailed analysis of the nmr spectrum is given in the discussion.

The relative alcohol, 2,2,3-triphenylcyclobutanol-1- d , was prepared in an identical manner but substituting lithium aluminum deuteride for lithium aluminum hydride.

A recent paper⁴⁹ gives mp 144–146° from methanol for the undeuterated alcohol.

(49) R. Huisgen and L. A. Feiler, *Chem. Ber.*, 102, 3391 (1969). The five following articles by Huisgen and coworkers contain additional material on diphenylketene cycloadditions.

Stereochemistry of Halogen Azide Additions to Olefins. The Stability of Three-Membered Iodonium vs. Bromonium Ions¹

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Abstract: The reaction of iodine azide and bromine azide with olefins in polar solvents was studied with a view toward the stereochemistry of the addition. Specifically, *cis*- β -deuteriostyrene (**6**) was used as a substrate to elucidate the properties of three-membered ring iodonium and bromonium ion intermediates. Thus, addition of IN_3 proceeded stereospecifically to **6** as evidenced by the exclusive formation of α -azido-*trans*- β -deuteriostyrene **10** on elimination of HI from the adduct. Though stereospecific *anti* addition of bromine azide was observed with *cis*- and *trans*-2-butene as well as with 2-cholestene, BrN_3 addition to **6** led to a 1:1 mixture of *cis*- and *trans*- α -azido- β -deuteriostyrene, indicating the involvement of a benzylic cation. The free-radical addition of BrN_3 to **6** indicates the reaction to be stereorandom and hence to involve no bridging of the intermediate radical by the azide group.

The addition of iodine azide (IN_3) to unsaturated compounds has been shown to be a highly regioselective² as well as stereoselective method of introduction of azide functions into organic molecules.³ This selectivity has been explained in terms of the formation of the three-membered ring halonium ion inter-

(1) (a) Stereochemistry, LIII. For the preceding paper in the series see A. Hassner, *Intra-Sci. Chem. Rep.*, 4, in press; (b) presented in part before the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 2, 1968, Paper P-81.

(2) *Regio* is used to denote directive effects in bond making or breaking: A. Hassner, *J. Org. Chem.*, 33, 2684 (1968).

(3) (a) F. W. Fowler, A. Hassner and L. A. Levy, *J. Amer. Chem. Soc.*, 89, 2077 (1967); (b) A. Hassner and F. W. Fowler, *J. Org. Chem.*, 33, 2686 (1968).

mediate which is opened regiospecifically and from the backside by azide ions. With phenyl-substituted olefins **1** opening of the iodonium ion always occurs at the benzylic carbon suggesting the possibility that equilibration of **2** with an open benzyl cation **3** may be occurring. Whereas iodonium ion **2** would be opened with inversion to the *erythro* isomer of **4**, carbonium ion **3** could become planar and convert to **5** by rotation, in which case a mixture of diastereomers should result.

The *anti*⁴ stereochemistry observed in IN_3 additions to β -substituted styrenes³ can be explained as proceeding

(4) We prefer to use *cis* and *trans* for configurational assignments and *syn* and *anti* describing transformations during chemical processes.