

which was pure by glc (SE-30, 230°): nmr δ 7.0–6.3 (cm, Ar), 3.60 (s, OCH₃), 2.9–2.3 (cm, H₁, H₄), 2.0–1.4 (cm, H₂, H₃).

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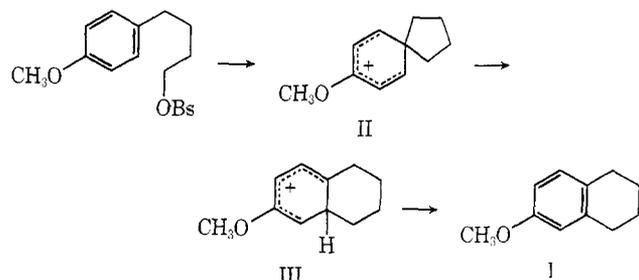
Formolysis of 4-(*p*-Methoxyphenyl)butyl *p*-Bromobenzenesulfonate

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Abstract: That fraction of the formolysis of 4-(*p*-methoxyphenyl)butyl *p*-bromobenzenesulfonate leading to 6-methoxytetralin proceeds through a symmetrical intermediate to the extent of 69.5% and through an unsymmetrical intermediate to the extent of 30.5%. The secondary deuterium isotope effect for the partition of the symmetrical intermediate is about 10%.

Winstein and his collaborators¹ have studied the solvolysis of a number of ω -aryl alkyl *p*-bromobenzenesulfonates and in the case of the formolysis of the 4-(*p*-methoxyphenyl)butyl ester showed that somewhat more than half of the product was 6-methoxytetralin (I).² The formation of this substance was ascribed to aryl participation to form an Ar₁-5 intermediate II which proceeded, presumably through



the intermediate III, to I. Aryl participation in the transition state leading to II was recognized as not large, however, on the basis of several criteria. (1) Rate enhancement over unassisted solvolysis was only a factor of 1.77 and is very much smaller than the rate enhancement produced by a *p*-methoxy group in, for example, bromination, where the rate enhancement is *ca.* 10¹⁰.³ (2) The low entropy of activation (-16.1 eu) is characteristic of unassisted rather than assisted solvolyses.⁴

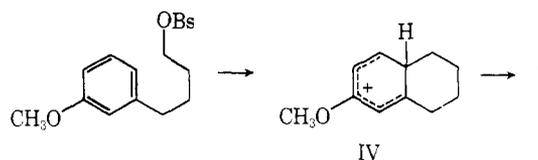
It appears to have been tacitly assumed by Winstein that 4-(*p*-methoxyphenyl)butyl *p*-bromobenzenesulfonate proceeds to 6-methoxytetralin largely if not exclusively through intermediate II, whereas the corresponding *m*-methoxyphenyl compound yielded the same tetralin through intermediate IV, formed by Ar₂-6 participation.

(1) S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956); S. Winstein, *Chem. Ind. (London)*, 562 (1954); S. Winstein and R. Baird, *J. Amer. Chem. Soc.*, **79**, 756 (1957); and especially R. Heck and S. Winstein, *ibid.*, **79**, 3105, 3114 (1957).

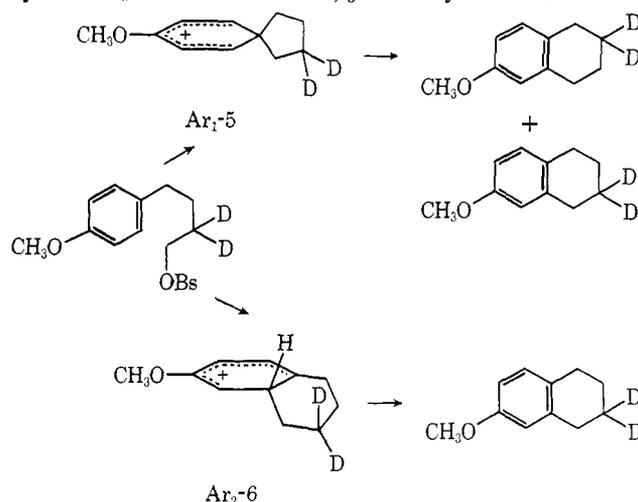
(2) Referred to in Winstein's papers as 7-methoxytetralin.

(3) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 1764 (1951).

(4) S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, **78**, 4801 (1956).



Haddon and Jackman,⁵ however, have recently reported the formolysis of 4-(*p*-methoxyphenyl)butyl-2,2-*d*₂ *p*-bromobenzenesulfonate (as well as that of the 4-(*p*-tolyl)-1-butyl-1,1-*d*₂ and -3,3,4,4-*d*₄ *p*-bromobenzenesulfonates). In the former case, the results were interpreted as indicating that 73.8% of that fraction of the solvolysis leading to 6-methoxytetralin (36%) went by the Ar₁-5 route and 26.2% went by the Ar₂-6 route.



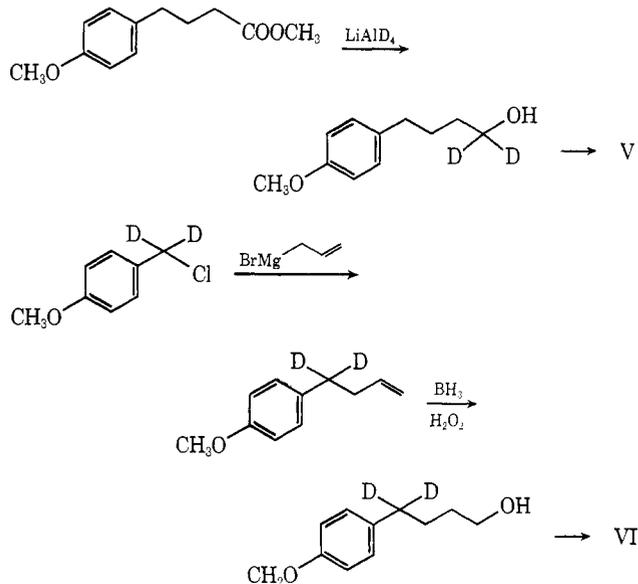
We had completed⁶ a study of the formolysis of the very closely related 4-(*p*-methoxyphenyl)butyl-1,1-*d*₂ *p*-bromobenzenesulfonate when the publication of Haddon and Jackman appeared, and have more recently studied the 4-(*p*-methoxyphenyl)butyl-4,4-*d*₂ *p*-bromobenzenesulfonate, and present our results here.

(5) V. R. Haddon and L. M. Jackman, *J. Amer. Chem. Soc.*, **93**, 3832 (1971).

(6) D. L. Frank, Ph.D. Dissertation, University of Rochester, 1970; *Diss. Abstr. Int. B*, **32**, 1446 (1971).

Methyl 4-(*p*-methoxyphenyl)butyrate was reduced with lithium aluminum deuteride to yield the corresponding butanol-1,1-*d*₂ which was converted to its *p*-bromosulfonate⁷ V.

4-(*p*-Methoxyphenyl)butanol-4,4-*d*₂ was prepared from anisyl- α,α -*d*₂ chloride by a modification of the sequence reported by Liedtke, Gerrard, Diekman, and Djerassi⁸ for the preparation of 4-phenylbutyraldehyde-4,4-*d*₂, omitting of course the final oxidation, and was converted to its *p*-bromobenzenesulfonate VI.



Formolysis of V (98.4% *d*₂, 1.6% *d*₁) and VI (97.4% *d*₂, 2.0% *d*₁)⁹ in dry formic acid containing a small amount of sodium formate at 70° for 48 hr (Winstein's conditions) gave, after lithium aluminum hydride reduction and column chromatography, 6-methoxytetralin-*d*₂ in 40% yield and the starting alcohol¹⁰ in 29% yield. In each case the position occupied by the two deuterium atoms in the 6-methoxytetralin produced was ascertained by the following series of reactions.

Since the equilibration of the β,γ -unsaturated ketone VII to the α,β -unsaturated ketone VIII allows the deuterium atoms at the 8 position but not those at the 5 position to enolize, the deuterium content at C₈ can be determined from the loss of deuterium on treatment with either acid or base of the deuterated ketone VII. The results of these degradations and equilibrations are summarized in Tables I and II.

Discussion

This work was originally undertaken to ascertain whether the intermediate in the formation of 6-methoxytetralin in these solvolyses was symmetrical, perhaps of

(7) The reaction sequence is essentially that of R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3105 (1957), except that the methyl ester rather than the acid was used in the lithium aluminum deuteride reduction.

(8) R. J. Liedtke, A. F. Gerrard, J. Diekman, and C. Djerassi, *J. Org. Chem.*, **37**, 776 (1972).

(9) All deuterium determinations were carried out by mass spectrometry (see Experimental Section). In the above two cases (V and VI) the deuterium contents were assumed to be the same as those of the corresponding acetates, since the flat-top peaks required for these analyses could not be obtained with the brosylates, and the parent alcohols gave varying ratios of peak heights corresponding to *m* (molecular ion) and *m* - 2, whereas the acetates yielded consistent figures.

(10) The nmr spectrum of this recovered alcohol showed no protons at carbon 1, in confirmation of the conclusion of Heck and Winstein¹ that the open-chain formate produced is derived only from nonassisted formolysis.

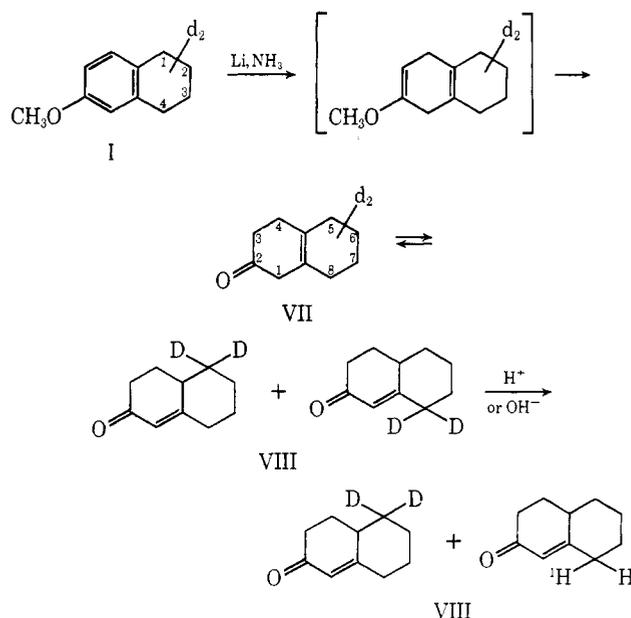


Table I. Formolysis of 4-(*p*-Methoxyphenyl)butyl-1,1-*d*₂ (V) and -4,4-*d*₂ (VI) *p*-Bromobenzenesulfonates

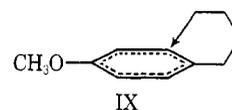
| Starting material | 6-Methoxytetralin | | VII | | VIII | | |
|-------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| | % <i>d</i> ₂ | % <i>d</i> ₁ | % <i>d</i> ₂ | % <i>d</i> ₁ | % <i>d</i> ₂ | % <i>d</i> ₁ | % <i>d</i> ₀ |
| V | 97.6 | 1.98 | 98.0 | 2.3 | 35.6 ^a | 0.8 ^a | 63.2 ^a |
| VI ^c | | | 96.3 | 2.4 | 34.6 ^b | 1.4 ^b | 63.5 ^b |
| | | | | | 64.5 ^a | 1.5 ^a | 34.3 ^a |

^a After equilibration of VII with 50-50% (vol.) ethanol-5% sulfuric acid at 80°. ^b After equilibration of VII with 30% dioxane-70% 0.3 M potassium hydroxide at 50°. ^c Equilibration with base, shown to give the same results as equilibration with acid in the case of V, was not used with VI inasmuch as it leads to much loss of material by side reactions (self-condensation?).

Table II. Partition of Deuterium between Position 1 and 4 of 6-Methoxytetralin from V and VI

| Starting material | VII atoms D/molecule | VIII atoms D/molecule | Fraction of D | |
|-------------------|----------------------|-----------------------|---|---|
| | | | lost (4,4- <i>d</i> ₂ + 4- <i>h</i> ,4- <i>d</i>) | retained (1,1- <i>d</i> ₂ + 1- <i>h</i> ,1- <i>d</i>) |
| V | 1.98 | 0.72 | 0.636 | 0.364 |
| VI | 1.95 | 1.30 | 0.331 | 0.669 |

the Ar₁-5 type, or unsymmetrical, perhaps of a π complex type, IX.¹¹

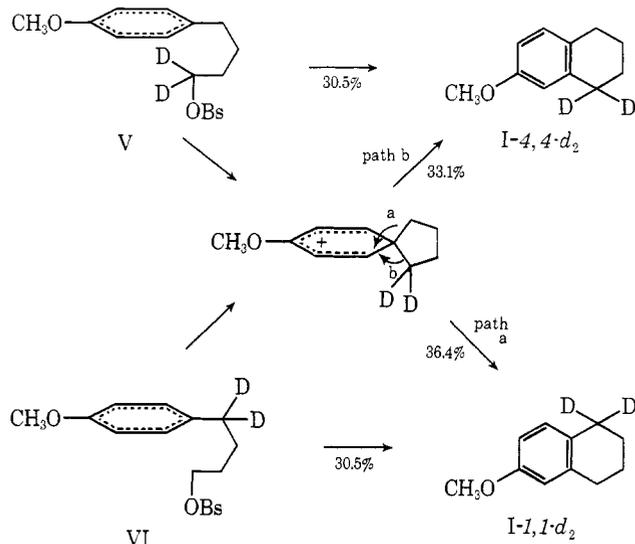


The results obtained with V and VI show at once that a substantial fraction of the product must be formed from a symmetrical intermediate. A closer look at the results allows a dissection of the reaction into its several paths and also allows an estimate of the isotope effect on the partition of the symmetrical intermediate to be made.

If one makes the eminently reasonable assumptions in the case of V that (1) 1-1,1-*d*₂ (and -1-*h*,1-*d*) arises only from :CH₂-R migration in a symmetrical intermediate

(11) The question as to whether the intermediate was symmetrical and of the Ar₁-5 type or unsymmetrical and of a π complex type arose during a discussion between one of us and Professor H. C. Brown some years ago.

and that (2) I-4,4- d_2 (and -4- $h,4-d$) represents the sum of :CD₂-R (and :CHD-R) migration in a symmetrical intermediate plus direct substitution from an unsymmetrical intermediate, and in the case of VI that (1) I-1,1- d_2 (and -1- $h,1-d$) represent the sum of :CH₂-R migration in a symmetrical intermediate plus direct substitution from an unsymmetrical intermediate and that (2) I-4,4- d_2 (and -4- $h,4-d$) arises only from :CD₂-R (and :CHD-R) migration in a symmetrical intermediate,¹² then that fraction of V which proceeds to I-1,1- d_2 is 36.4%; that fraction of VI which proceeds to I-4,4- d_2 is 33.1%; that fraction of V which proceeds by an unsymmetrical path is 63.6% - 33.1% = 30.5%, and that fraction of VI which proceeds by an unsymmetrical path is 66.9% - 36.4% = 30.5%. These relationships are summarized below.¹³

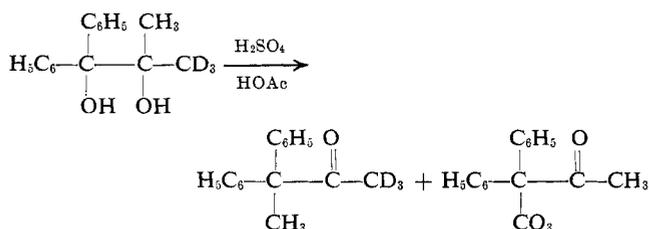


The values for the conversion of the symmetrical intermediate to I-4,4- d_2 (33.1%) and to I-1,1- d_2 (36.4%) allow one to estimate that the secondary deuterium isotope effect for this partition ($36.4/33.1 = 1.10$) is about 10%.¹⁴

(12) A referee has pointed out that there is an additional assumption implicit in our treatment of these data, *i.e.*, that the fraction of product derived from a symmetrical intermediate followed by R-CH₂: migration is the same for V (where it is directly measurable) and for VI, and that the fraction of product derived from a symmetrical intermediate followed by R-CD₂: migration is the same for VI (where it is directly measurable) and for V. We are grateful for this and a number of other very helpful comments of the referee.

(13) The symmetrical intermediate is for convenience depicted as of the Ar₁-5 type, but it should be emphasized that no direct evidence for the structure of the intermediate exists, nor do these results support such a structure, although they are consistent with it. All one can conclude from these experiments and from those of Haddon and Jackman is that in the intermediate, positions 1 and 4 of the butyl chain become equivalent.

(14) We have not found examples of reactions exhibiting secondary deuterium isotope effects which are strictly comparable to these solvolyses, but the following reaction has been studied (W. M. Schubert and P. M. LeFevre, *J. Amer. Chem. Soc.*, **91**, 7746 (1969)) and shows an



isotope effect of 1.232. If one assumes the effect per deuterium is additive, migration of CD₂-R might be expected to show an isotope effect of about 1.16.

Our values for the extent of solvolysis going by the symmetrical route (33.1% + 36.4% = 69.5%) and by the unsymmetrical route (30.5%) are similar to, but not identical with, those obtained by Haddon and Jackman⁵ (73.8 and 26.2%, respectively). Both studies show that although a substantial fraction of the reaction producing 6-methoxytetralin goes through a symmetrical intermediate, perhaps of the Ar₁-5 type, a not inappreciable fraction also goes through an unsymmetrical intermediate, perhaps of the Ar₁-6 type.¹⁵ The fact that the latter reaction competes successfully with the former is further evidence of the rather small effect of the methoxyl group on the transition states of these reactions, since a transition state strongly resembling II would surely be better able to accommodate the positive charge than would one resembling III.

Experimental Section

General. Infrared spectra were recorded on a Perkin-Elmer infrared 137 spectrophotometer and were calibrated using the 1601-cm⁻¹ absorption of polystyrene film. Unless otherwise recorded, spectra were taken from films (neat) between sodium chloride plates.

Nuclear magnetic resonance spectra were recorded on a Jeolco C60-HL spectrometer using deuteriochloroform as solvent and tetramethylsilane as an internal standard.

Thin-layer chromatograms were taken on microscope slides coated with Merck Silica Gel G and were visualized with iodine vapor. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Mass spectra were determined on an Hitachi Perkin-Elmer RMU6E mass spectrometer fitted with a Visicorder light beam recorder. For deuterium analyses, such spectra were recorded at an ionizing chamber temperature of 200°, pressure 2-6 × 10⁻⁷ mm with widened entrance (0.30 mm) and exit (0.55 mm) slits. Scan speeds were reduced and ionizing potential was kept at 14 eV. Under these conditions, molecular ions are produced without fragmentation and flat-topped peaks are observed, allowing accurate determination of peak heights. Deuterium constants were calculated by computer¹⁷ solutions of the following simultaneous equations, in which H_m , H_{m+1} , etc., are the peak heights at $m/e =$

$$H_m = d'_0$$

$$H_{m+1} = d'_0(m_1) + d'_1$$

$$H_{m+2} = d'_0(m_2) + d'_1(m_1) + d'_2$$

$$H_{m+3} = d'_1(m_2) + d'_2(m_1) + d'_3$$

$m, m + 1, \text{etc.}$, in the deuterated species and $d'_0, d'_1, \text{etc.}$, are raw numbers proportional to the mole fractions of undeuterated, mono-deuterated, etc., compounds and in which $m_1 = H_{m+1}/H_m$, $m_2 = H_{m+2}/H_m$ for the undeuterated species.

Methyl 4-(*p*-Methoxyphenyl)butyrate. To 9.3 g (0.048 mol) of 4-(*p*-methoxyphenyl)butyric acid and 0.1 g of *p*-toluenesulfonic acid was added 50 ml of methanol dried over 3A molecular sieves. The mixture was heated to reflux for 24 hr, the condensate being returned through a Soxhlet thimble charged with freshly dried sieves of the same type. The methanol was removed at reduced pressure, and the residue was dissolved in 50 ml of ether, and washed three

(15) These results do not allow a choice between the Ar₂-6 intermediate III and a π -complex (IX ?) intermediate for the unsymmetrical component of these solvolyses. Neither do they allow a choice between the Ar₁-5 intermediate II and a pair of rapidly equilibrating ions analogous to those suggested by Brown¹⁶ for the β -*p*-methoxyphenethyl solvolysis intermediate, although the latter can serve only if they are never intercepted by solvent, since the 4-(*p*-methoxyphenyl)butyl alcohol recovered shows no deuterium scrambling.¹⁰

(16) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Amer. Chem. Soc.*, **89**, 370 (1967). More recent work indicates that the equilibrating ion concept fails to explain adequately even the β -phenethyl cases: H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *ibid.*, **92**, 5244 (1970).

(17) We are grateful to Drs. L. E. Friedrich and Gary Schuster for providing us with the program for these calculations and for many helpful discussions.

times with 30-ml portions of potassium bicarbonate solution, once with water, and finally with brine. The ethereal solution was then dried and evaporated to yield 9.3 g of an oil. Distillation gave 8.6 g (86%) of the purified ester: bp 105–110° (0.25 mm); n_D^{20} 1.5050; ir 1748 cm^{-1} (C=O); nmr 1.60–2.70 (m, 6 H, CH_2), 3.54 and 3.64 (s, 6 H, OCH_3), 6.50–7.00 ppm (q, 4 H, ArH).

Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$: C, 69.20; H, 7.75. Found: C, 69.03; H, 7.60.

4-(*p*-Methoxyphenyl)-1-butanol-1,1- d_2 . To a stirring solution of 1.0 g (0.024 mol) of lithium aluminum deuteride in 50 ml of dry ether was added 9.93 g (0.048 mol) of methyl 4-(*p*-methoxyphenyl)-butyrate in 20 ml of dry ether. After 2-hr reflux, the excess LiAlD_4 was destroyed by addition of a saturated solution of rochelle salts, and the mixture was poured into 100 ml of 5% hydrochloric acid. The ethereal layer was separated, and the aqueous layer was extracted with three fresh portions of ether. The combined ethereal extracts were washed two times with bicarbonate solution, with water, and finally with brine. The ethereal solution was then dried and evaporated to yield 8.07 g of an oil, which upon distillation gave 7.76 g (89%) of the deuterated alcohol: bp 110–115° (0.35 mm); n_D^{20} 1.5191; ir 3230 cm^{-1} (O–H), 2170 and 2066 cm^{-1} (C–D); nmr 1.48–1.75 (m, 4 H, CH_2), 3.71 (s, 3 H, OCH_3), 6.61–7.15 ppm (q, 4 H, ArH).

4-(*p*-Methoxyphenyl)-1-butyl Acetate. To 0.079 g (0.044 mol) of 4-(*p*-methoxyphenyl)-1-butanol in 5 ml of methylene chloride were added 0.5 g of sodium bicarbonate and 0.5 ml of acetyl chloride. After the mixture was stirred for 20 min, the ebullition had ceased and the mixture was poured into 20 ml of saturated aqueous bicarbonate and stirred 15 min. The methylene chloride layer was then removed, washed with water, and dried to yield 0.10 g (97%) of the ester: bp 110–112° (0.3 mm); n_D^{20} 1.4997; ir 1730 cm^{-1} (C=O); nmr 1.50–1.75 (m, 4 H, CH_2), 1.95 (s, 3 H, CH_3CO), 2.35–2.65 (m, 2 H, ArCH_2), 3.69 (s, 3 H, OCH_3), 3.82–4.10 (m, 2 H, CH_2), 6.55–7.10 ppm (q, 4 H, ArH). Thin-layer chromatography revealed no trace of starting material.

Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_3$: C, 70.24; H, 8.16. Found: C, 70.38; H, 8.20.

The deuterated acetate was prepared following the same procedure. The absorption at 3.8–4.1 ppm, due to the protons on the α carbon, was absent in the nmr.

4-(*p*-Methoxyphenyl)-1-butyl-1,1- d_2 *p*-Bromobenzenesulfonate (V). To 5.88 g (0.032 mol) of 4-(methoxyphenyl)-1-butanol-1,1- d_2 in 60 ml of pyridine at -15° was slowly added 12.35 g (0.048 mol) of *p*-bromobenzenesulfonyl chloride in 30 ml of ice-cooled pyridine. The mixture was maintained at -15° for 24 hr, after which it was added to 600 ml of ice-water. The aqueous solution was extracted with three 100-ml portions of ether. The combined extracts were washed successively with 150-ml portions of 5% hydrochloric acid, water, saturated bicarbonate solution, and brine. Drying and evaporation left an oil which was triturated with petroleum ether at 0° . Scratching produced 11.46 g (88%) of the crude product, off-white prisms melting at 41–44°. One recrystallization from ether-petroleum ether gave 10.43 g (80%) of the purified brosylate: mp 44–46°; nmr 1.50–1.75 (m, 4 H, CH_2), 2.30–2.70 (m, 2 H, ArCH_2), 3.75 (s, 3 H, OCH_3), 6.63–7.10 (q, 4 H, ArH), 7.66 ppm (s, 4 H, ArH). A crude estimate of deuterium content by the subtraction technique from data obtained during a regular mass spectral scan (narrow slits, fast scan) gave 97% d_2 , 3% d_1 .

6-Methoxyl-1,2,3,4-tetrahydronaphthalene- d_2 (I). One liter of formic acid (Baker, 88%) was allowed to stand over 100 g of boric anhydride for 3 days. The acid was then decanted and distilled at reduced pressure to give 650 ml of dry formic acid, to which 1.316 g (0.02 mol) of sodium formate and 10.43 g (0.026 mol) of 4-(*p*-methoxyphenyl)-1-butyl-1,1- d_2 brosylate (V) were added. The mixture was heated at 70° for 48 hr. About half of the formic acid solution was then removed at diminished pressure. The remaining solution was diluted with an equal volume of water, and the solution was extracted with three 20-ml portions of pentane. The combined pentane extracts were washed with a saturated solution of sodium bicarbonate and with brine, then dried, and evaporated to yield 4.48 g (95%, calculated from product ratios) of a yellowish oil, a mixture of the tetralin and formate ester of the starting alcohol. This oil was dissolved in 25 ml of dry ether, and the solution was injected slowly into a stirring, ice-cooled suspension of 2 g of lithium aluminum hydride in 50 ml of ether. The solution was stirred for 1 hr; the excess LiAlH_4 was destroyed with a saturated solution of rochelle salts. Filtration followed by evaporation of the filtrate gave 3.78 g (85%, based on brosylate and calculated from product ratios) of a yellowish oil, a mixture of the tetralin and alcohol. This oil was chromatographed on grade 1 neutral Woelm

alumina. The column was first eluted with toluene, which removed 1.68 g (40% based on brosylate) of the deuterated tetralin: bp 71–74° (0.35 mm); n_D^{20} 1.5401; nmr 1.55–1.95 (m, 4 H, CH_2), 2.40–2.85 (broad d, 2 H, ArCH_2), 3.65 (s, 3 H, OCH_3), 6.45–6.97 ppm (m, 3 H, ArH). The broad absorption at 2.40–2.90 ppm in the undeuterated tetralin integrated to four protons.

Table III. Deuterium Analysis of Tetralin

| Mass | No. of deuterium | % calcd |
|------|------------------|--------------|
| 162 | 0 | 0 |
| 163 | 1 | 1.98 ± 0.014 |
| 164 | 2 | 97.61 ± 0.15 |
| 165 | 3 | 0.10 ± 0.023 |
| 166 | 4 | 0.32 ± 0.014 |

The column was then eluted with a 50% methylene chloride–50% methanol solution to give 1.392 g (29%) of the starting alcohol, its identity being confirmed by ir and nmr spectra comparison with the original compound.

2-Keto-1,2,3,4,5,6,7,8-octahydronaphthalene- d_2 (VII). The following procedure was conducted under a nitrogen atmosphere. Ether (10 ml) dried over LiAlH_4 was distilled directly into a predried flask containing 0.50 g (3.05 mmol) of 6-methoxyl-1,2,3,4-tetrahydronaphthalene- d_2 . After addition of 2.92 ml of dry *tert*-butyl alcohol, the flask was fitted with a Dewar condenser and bath. Dry Ice and acetone were added to both as gaseous ammonia was passed through the system. After approximately 15 ml of ammonia had condensed, the bath was removed and the nitrogen atmosphere restored. Lithium (0.10 g, 0.014 mol), cleaned by soaking in methanol until free of its waxy coating, was added piecewise. The solution, after lithium addition, was intensely blue. The mixture was allowed to react for 5 hr, after which 1 ml of methanol was added dropwise, and the ammonia was allowed to escape.

Work-up was performed in a glove bag under nitrogen. To the remaining solution was added 25 ml of water, and the mixture was extracted with three 20-ml portions of ether. Evaporation of the dried ethereal extracts gave 0.491 g (97%) of an oil: ir 2165 and 2079 cm^{-1} (C–D), 1718 and 1675 cm^{-1} (C=C); nmr 1.50–2.30 (m, 6 H, C=CCH), 2.50–2.80 (broad s, 4 H, C=CCHC=C), 3.54 (s, 3 H, OCH_3), 4.50–4.75 ppm (broad s, 1 H, C=CH).

To this oil under a nitrogen atmosphere was added 50 ml of a saturated solution of sodium bisulfite in a 25:75 ethanol–water solution. The mixture was stirred vigorously under nitrogen for 2 days, after which the precipitate which had formed was collected, washed with ether, and dried to yield 0.424 g (54%) of the bisulfite addition product. This was added to a solution of 5 g of sodium carbonate in 15 ml of water and stirred for 15 min. The mixture was extracted with three 20-ml portions of ether which were combined, dried, and evaporated to yield 0.211 g of an oil. Distillation on a molecular still gave 0.197 g (78% based on the bisulfite product) of the β,γ -ketone mixture: tlc revealed one spot on silica gel in 50% ethyl acetate–50% benzene (v/v), R_f 0.54; ir 2174 and 2096 cm^{-1} (C–D), 1740 cm^{-1} (C=O), deuterium content 98% d_2 , 2.3% d_1 . The 2,4-dinitrophenylhydrazone was prepared in alcoholic sulfuric acid, and after two crystallizations from alcohol had mp 175–176° (reported for the undeuterated analog, 176–177°¹⁸).

2-Keto-2,3,4,5,6,7,8,10-octahydronaphthalene- d_2 and - d_0 (VIII). **Acid Wash.** To a solution of 10 ml of ethanol and 10 ml of 5% sulfuric acid was added 0.165 g (1.1 mmol) of the β,γ -unsaturated ketone. Aliquots of 3 ml were withdrawn from the refluxing solution after 4, 12, 24, and 32 hr (Table IV). The standard procedure to recover the ketone was as follows: the ethanol was removed at reduced pressure, the residue was diluted with an equal volume of water, and the resulting turbidity was extracted with three 10-ml portions of ether. The combined ethereal extracts were dried and evaporated to give 25-mg samplings of the crude product. The first two samples were not purified by thick-layer chromatography prior to recording their mass spectra; however, the mass spectra of the last two were taken both before and after thick-layer purification (there was little difference except in the d_4 peak). Chromatography was done on 5 cm × 21 cm glass plates coated with a 0.10-mm layer of silica gel. The eluting solvent was

(18) A. J. Birch, *J. Chem. Soc.*, 593 (1946).

Table IV. Deuterium Content of VIII during Acid Wash at 80°

| | % deuterium incorporation | | |
|-----------------|---------------------------|-------------|-------------|
| | d_0 | d_1 | d_2 |
| 4 ^a | 21.8 ± 0.24 | 32.2 ± 0.24 | 46.0 ± 0.24 |
| 12 ^a | 58.2 ± 0.92 | 6.9 ± 0.13 | 34.7 ± 0.92 |
| 24 ^b | 62.3 ± 0.50 | 1.4 ± 0.07 | 35.2 ± 0.50 |
| 32 ^b | 63.2 ± 0.50 | 0.8 ± 0.07 | 35.6 ± 0.50 |

^a Truncated at d_4 . ^b Purified by thin layer chromatography. Values at d_3 and d_4 are negligible.

a 50% ethyl acetate–50% benzene solution. Visualization of the area to be collected was accomplished with a Mineralite ultraviolet lamp. The nonfluorescent band R_f 0.47–0.66 was removed and eluted with 50% methylene chloride–50% methanol. Removal of the solvent left 20.2 mg (81%) of an oil: ir 1666 (con. C=O), 1709 (uncon. C=O), 1618 cm^{-1} (C=C). The R_f of this material on silica gel was identical with the R_f value of the undeuterated α,β -unsaturated ketone. The 2,4-dinitrophenylhydrazone of the deuterated material was prepared after the final wash; after one recrystallization from ethanol its melting point was 168–169° (lit.¹⁹ 168–169°).

Base Wash I. The β,γ -unsaturated ketone (0.19 g, 1.3 mmol) was added to 3 ml of dioxane and 7 ml of 0.25 M potassium hydroxide.

Table V. Deuterium Content of VIII during Base Wash (30% Dioxane–70% 0.25 M KOH) at 50°

| Hr washed | % deuterium | | |
|-----------------|-------------|-------------|-------------|
| | d_0 | d_1 | d_2 |
| 36 ^a | 48.0 ± 0.10 | 16.0 ± 0.11 | 35.6 ± 0.11 |
| 60 ^a | 63.5 ± 0.41 | 1.4 ± 0.06 | 34.6 ± 0.41 |

^a Purified by thick layer chromatography. Values at d_3 and d_4 are negligible.

The solution was heated at 50° with stirring. After 36 hr, the entire reddish-brown mixture was diluted with 20 ml of water and extracted with three 30-ml portions of ether to yield 0.18 g of a yellowish oil. The thin-layer chromatogram revealed a complex mixture of products, but the spot corresponding to the α,β -unsaturated ketone was apparent. Distillation in a molecular still produced only 66 mg (36%) of lower boiling material, corresponding to the desired product by tlc and ir. Nevertheless a portion of the distilled material was further purified by thick-layer chromatography as previously described. The product was identified by ir spectral comparison with the ketone obtained by acid isomerization, and by R_f value. The remaining distilled material (55 mg) was added to 3 ml of dioxane and 7 ml of 0.25 M potassium hydroxide and heated at 50° for an additional 24 hr. Similar work-up gave 50 mg of a light yellow oil, the tlc of which again revealed the complex product mixture as previously described. The material was further purified by thick-layer chromatography to give a sufficient quantity of the purified ketone for mass spectral analysis.

Base Wash II. The β,γ -unsaturated ketone (0.141 g, 0.93 mmol) was added to 3 ml of 95% ethanol and 6 ml of 0.3 M potassium hydroxide and stirred at 25° for 3 days. The ethanol was then

Table VI. Deuterium Content of VIII during Base Wash (30% Ethanol–70% 0.3 M KOH) at 25°

| Days washed | % deuterium | | |
|----------------|-------------|-------------|-------------|
| | d_0 | d_1 | d_2 |
| 3 ^a | 43.2 ± 0.13 | 19.5 ± 0.14 | 37.4 ± 0.14 |
| 6 ^a | 57.8 ± 0.99 | 6.2 ± 0.15 | 35.4 ± 0.99 |
| 9 ^b | 60.3 ± 0.41 | 2.6 ± 0.06 | 35.0 ± 0.41 |

^a Truncated at d_4 . ^b Purified by thin-layer chromatography. Values at d_3 and d_4 are negligible.

removed, the remaining mixture diluted with an equal volume of water, and the resulting turbidity extracted with three 15-ml por-

(19) H. H. Zeiss and W. B. Martin, Jr., *J. Amer. Chem. Soc.*, **75**, 5935 (1953).

tions of ether. The combined extracts were dried and evaporated to yield 0.132 g of a yellowish oil. The previously described product mixture was observed on tlc, but it was not further purified prior to recording its mass spectrum. The recovered oil was subjected to a second and a third 3-day wash as described. The product was purified by thick-layer chromatography after the third wash, and was identified by ir spectral comparison and R_f value, as well as mass spectrometry.

***p*-Methoxybenzyl- α,α - d_2 Alcohol.** To a stirred solution of 0.5 g (0.012 mol) of LiAlD_4 in 50 ml of anhydrous ether, 3 g (0.018 mol) of methyl *p*-methoxybenzoate²⁰ in 10 ml of anhydrous ether was added dropwise. The solution was refluxed 5 hr under dry nitrogen. Excess hydride was destroyed by adding 5 ml of D_2O . To the reaction mixture, 100 ml of 5% sulfuric acid was added. The aqueous layer was washed with ether. The ether fractions were combined and dried; the ether was removed on a rotary evaporator to yield 2.34 g (95.5%) of the deuterated alcohol: n_D^{25} 1.554; ir 3320 (OH), 2075–2370 cm^{-1} (CD); nmr 3.40 (s, 1 H, OH), 3.78 (s, 3 H, OCH_3), 6.82–7.30 ppm (q, 4 H, ArH).

***p*-Methoxybenzyl- α,α - d_2 Chloride.** To 1.63 g (0.0129 mol) of *p*-methoxybenzyl- d_2 alcohol and 0.79 g (0.011 mol) of pyridine in 50 ml of chloroform, 0.75 ml of thionyl chloride in 10 ml of chloroform was added dropwise. The reaction mixture was stirred at 25° for 3 hr. After this period, 100 ml of water was added. The aqueous layer was removed, and the chloroform layer was washed with 5% sulfuric acid, 10% sodium bicarbonate, and brine. The chloroform layer was dried with magnesium sulfate and concentrated to yield 2.02 g (98.9%) of a clear oil: ir 965 and 640 cm^{-1} (CO_2Cl); nmr 3.75 (s, 3 H, OCH_3), 6.75–7.32 ppm (q, 4 H, ArH).

4-(*p*-Methoxyphenyl)-1-butene-4,4- d_2 . To a stirred solution of 0.012 mol of freshly prepared allyl magnesium bromide, 1.58 g (0.010 mol) of freshly prepared *p*-methoxybenzyl- α,α - d_2 chloride in 10 ml of ether was added dropwise. The reaction mixture was refluxed 2 hr, then hydrolyzed by adding enough saturated ammonium chloride to form a solid cake of inorganic salts. The ether layer was decanted, and the ether was removed at reduced pressure to yield 1.61 g (95.5%) of an oil: n_D^{25} 1.516; ir 1640, 1416, 990, 895 cm^{-1} (C=C); nmr 2.28–2.38 (m, 2 H, CH_2), 2.75 ppm (s, 3 H, OCH_3), 4.85–5.17 (m, 2 H, CH_2), 5.5–6.2 (m, 1 H, CH), 6.80–7.20 ppm (m, 4 H, ArH).

4-(*p*-Methoxyphenyl)-1-butanol-4,4- d_2 . To an ice cooled stirred suspension of 0.2 g (0.0061 mol) of NaBH_4 in 25 ml of THF containing 1 g (0.0067 mol) of 4-(*p*-methoxyphenyl)-1-butene-4,4- d_2 , 1.02 ml (0.00815 mol) of $\text{BF}_3 \cdot \text{etherate}$ in 5 ml of THF was added dropwise. After the addition the reaction was allowed to come to room temperature and was stirred for 2 hr. At the end of this period, the excess hydride was destroyed with water and 6 ml of 3 N NaOH and 30% H_2O_2 was added. The reaction mixture was warmed to 30–40°. After 24 hr, the reaction mixture was saturated with NaCl. The THF was removed under reduced pressure to yield 1.168 g (103%) of an oil: bp 285°; n_D^{25} 1.523; ir 3230 (OH), 2170 and 2066 cm^{-1} (C-D); nmr 1.10–1.75 (m, 4 H, CH_2), 3.45–3.80 (m, 2 H, CH_2), 3.78 (s, 3 H, OCH_3), 5.95 (s, 1 H, OH), 6.80–7.35 ppm (m, 4 H, ArH); deuterium content (97.4% d_2), (2.0% d_1). This substance was converted to its *p*-bromobenzenesulfonate VI as described for V.

Solvolysis of VI (97.4% d_2 , 2.0% d_1) was carried out as described above for its isomer V. The β,γ -unsaturated ketone VII so obtained contained 96.3% d_2 , 2.4% d_1 , and 1.5% d_0 .⁹ Equilibration of this substance with acid was carried out as described above and gave the results found in Table VII.

Table VII. Deuterium Content of VIII during Acid Wash at 80°

| Hr washed | % deuterium | | |
|-----------------|-------------|------------|------------|
| | d_0 | d_1 | d_2 |
| 14 | 33.6 ± 0.3 | 3.4 ± 0.05 | 61.9 ± 0.3 |
| 34 | 36.6 ± 0.3 | 1.2 ± 0.4 | 61.6 ± 0.3 |
| 54 ^a | 34.3 ± 0.3 | 1.5 ± 0.05 | 64.5 ± 0.3 |

^a Purified by thin-layer chromatography.

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(20) A. Ladenburg and A. Fitz, *Justus Liebigs Ann. Chem.*, **141**, 252 (1867).

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A Novel Photochemical 1,4-Phenyl Migration. The Role of the Second π Bond in the Di- π -methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry^{1,2}

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Abstract: In order to assess the role of the second π bond in the di- π -methane rearrangement, the photochemistry of 1,1,5,5-tetraphenyl-3,3-dimethyl-1-pentene was investigated. It was ascertained that neither the singlet nor the triplet of this tetraphenyl monoene rearranged in di- π -methane-like fashion. The absence of cyclopropane product contrasts dramatically with the known facile rearrangement of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene. While the triplet excited state of the tetraphenyl monoene was unreactive, the singlet rearranged to afford 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene in a novel 1,4-phenyl migration. Additionally, to a lesser extent, rearrangement occurred to afford 1,2,2,3-tetraphenyl-4,4-dimethylcyclopentane. The quantum yield for formation of the major product was $\phi = 0.00081$. That for the tetraphenyldimethylcyclopentane was $\phi = 0.0002$. An upper limit on the intrusion of any di- π -methane-type product could be set as 1/25th of this. Further, the low reactivity of the tetraphenylmonoene was found to derive from an inherently low rate of singlet rearrangement rather than a rapid excited-state decay. The rate of rearrangement of the singlet to give tetraphenyldimethylpentene was $k_r = 2.4 \times 10^7 \text{ sec}^{-1}$. This is indeed low compared with di- π -methane systems. The rate of all excited-state decay processes is $k_{dt} = 3.0 \times 10^{10} \text{ sec}^{-1}$. This, again, is low. From these data it is concluded that any di- π -methane-like rearrangement occurring must be even slower than the phenyl migration process. It is seen that the second π bond is a necessity for facile rearrangement.

Eight years ago we reported the rearrangement of barrelene to semibullvalene.³ It was quickly recognized that the rearrangement mechanism was characteristic of molecules which have two π groups bonded to a central sp^3 -hybridized carbon atom; we thus termed the reaction the di- π -methane rearrangement.^{3b,4} Since that time the rearrangement has proven extraordinarily general,⁵⁻⁹ and an ever increasing number of examples are being reported.¹⁰

One example which has been thoroughly studied is

(1) Paper LXXXIX of the series. For the previous paper on Mechanistic and Exploratory Organic Photochemistry, note H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *J. Amer. Chem. Soc.*, **96**, 4630 (1974).

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(7) H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971).

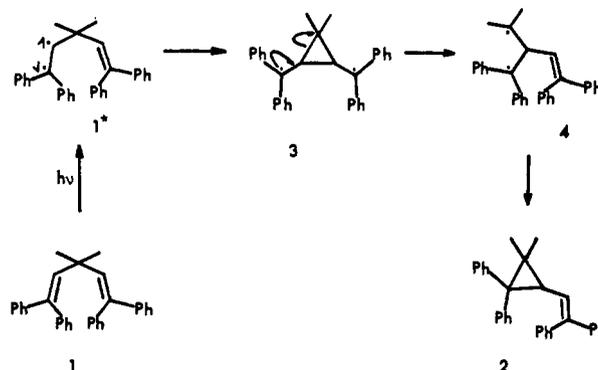
(8) H. E. Zimmerman, P. Baekstrom, T. Johnson, and D. W. Kurtz, *J. Amer. Chem. Soc.*, **94**, 5504 (1972).

(9) H. E. Zimmerman, R. J. Boettcher, and W. Braig, *J. Amer. Chem. Soc.*, **95**, 2155 (1973).

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that of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**1**) which rearranges to give 1,1-diphenyl-2,2-dimethyl-3-(2',2'-diphenylvinyl)cyclopropane (**2**).⁵ The mechanism we suggested⁵ is shown in Chart I. This begins

Chart I. Mechanism for the Photochemical Rearrangement of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene (**1**)



with bonding between the two π moieties of the singlet excited state. In contrast, Woodward and Hoffmann¹¹ have proposed that the reaction is a $\sigma 2_a + \pi 2_a$ or $\sigma 2_s + \pi 2_s$ process. In this mechanism only one π bond plays a role. The question posed then was whether the second π bond really is required for the reaction. An answer

(11) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 98-100.