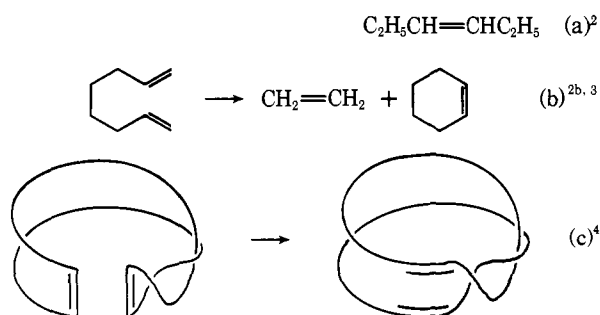# Mechanism of the Olefin Metathesis of 2,2'-Divinylbiphenyl

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Abstract: Tungsten- and molybdenum-catalyzed metatheses of mixtures of equal amounts of 2,2'-divinylbiphenyl-d_4 (Va) and unlabeled 2,2'-divinylbiphenyl (Vb) give after 1–2% reaction, besides phenanthrene, mixtures of $CH_2\!=\!CH_2$, $CH_2\!=\!CD_2$, and $CD_2\!=\!CD_2$ in ratios 1:2:1. The difference in the ratios of the d_0, d_2, and d_4 materials in the ethylene product and in the divinylbiphenyl precursor cannot be attributed to scrambling of the d_0-, d_2-, and d_4-divinylbiphenyls before appreciable amounts of ethylene evolve because the divinylbiphenyl recovered from the reaction mixtures still consisted of equal amounts of undeuterated and tetradeuterated material, with no appreciable additional dideuterated material. The disparity also cannot be ascribed to rapid scrambling of the ethylenes after they are initially formed because metathesis of undeuterated divinylbiphenyl in the presence of *trans*-dideuterioethylene does not give appreciable amounts of monodeuterated ethylene. The data are in Tables I and II. The results conflict with the conventional mechanism, depicted in eq 4, no matter whether the first or second step is rate determining. The results do agree with expectation based on the chain-reaction mechanism depicted in eq 1.

The olefin metathesis reaction, illustrated by reactions a–c, is effected by catalysts usually containing tungsten,

$$2CH_3CH\!=\!CHC_2H_5 \rightleftharpoons CH_3CH\!=\!CHCH_3 +$$

$$C_2H_5CH\!=\!CHC_2H_5 \quad (a)^2$$

$$\rightarrow CH_2\!=\!CH_2 + \quad (b)^{2b,\,3}$$

$$\rightarrow \quad (c)^4$$

molybdenum, or rhenium, and this, as well as much of whatever else is known about the reaction, has been summarized during the last 7 years in seven major review articles.[5] The general supposition has been that the mechanism of the reaction involves a species in which four carbons and a metal are bonded together, either as I or as the related II and III.
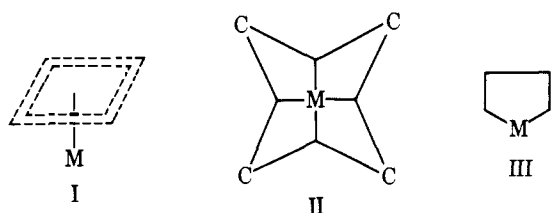
However, a recent paper from our laboratory[6] shows how the chain reaction in eq 1 accounts more satisfactorily than

$$(1)$$
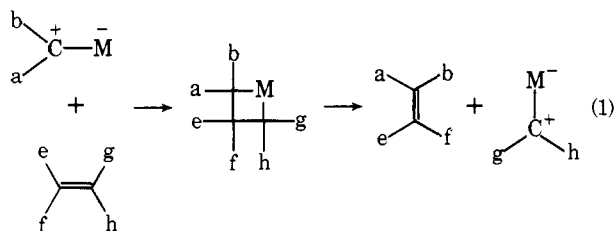
the conventional mechanism for the facts that led to the original supposition—(1) the gross structural change, (2) the absence of cyclobutanes as side products of the reaction, and (3) the failure of cyclobutanes to enter the reaction—as well as for the following: (4) at the start of reaction 2, the

predominance of the cross product (labeled C_{14}) over the conventional products (labeled C_{12} and C_{16}), (5) at the start of the seemingly similar reaction 3, the absence of

$$(2)$$

$$(3)$$
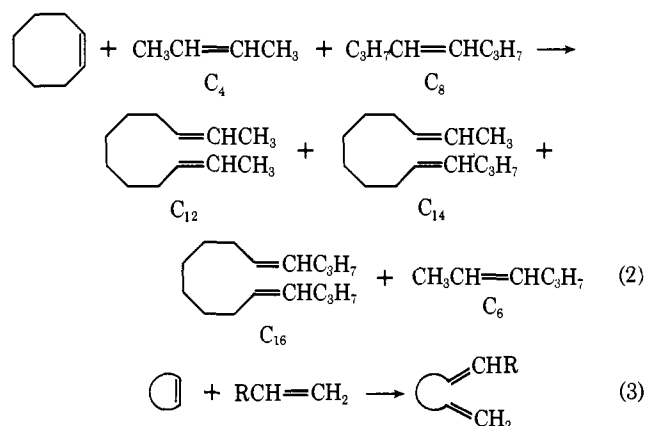
cross products, (6) the metathesis of acetylenes, (7) the stereochemistry of metathesis, (8) the high molecular weights of the polymers formed early in the metathesis of cycloalkenes, (9) the formation of similar products containing $(C_4H_6)_n$ fragments in metatheses of cycloocta-1,5-diene and cyclododeca-1,4,7-triene, and (10) initiation of metathesis by reagents that plausibly generate metal-carbenes. Also the kinetics, which were measured[7] as first order in the metal and of variable order in olefin (seemingly first order[8] at high olefin concentration and up to order 1.7 at low olefin concentration), are in accord with this proposal.[9]

The chain reaction mechanism had earlier been proposed by Hérisson and Chauvin[10] to account for a fact like (4) above (in their experiment the cross products did not predominate) and for fact 8, but they could not reconcile fact 5 or fact 9 with the mechanism,[11] and they did not consider the other facts. Their proposal was neglected for 4 years but has received considerable support recently. Casey and Burkhardt[12] and Cardin, Doyle, and Lappert[13] discovered demonstrations of the mechanism in their interpretation of the stoichiometric exchange of olefins with stable metal-carbene complexes. Dolgoplosk et al.[14] have recently demonstrated fact 10, for which two other experiments can be considered unrecognized demonstrations.[3a,15] Grubbs et al. reported experiments very similar to those presented below.[16,17] Muetterties adopted the mechanism in a recent discussion.[18]

Nevertheless, these explanations and demonstrations do not prove the chain mechanism since almost all the facts have also been explained using the conventional mechanism. Thus facts 4[6] and 8[5d] can be explained if the rate-determining step in olefin metathesis is step 2 in eq 4, not step

$$R_1CH\!=\!CHR_1 \quad\quad R_1CH \quad CHR_1$$

(4)
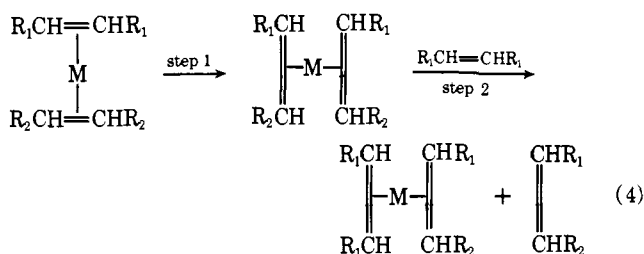
1; the explanation of fact 10 is ambiguous because there is no proof that the reactions that might generate carbenes actually do or that carbenes if formed are in fact the catalysts; and the stoichiometric exchange reactions of stable metal-carbenes with olefins might have nothing to do with olefin metathesis. The one fact that seems impossible to reconcile with the conventional mechanism is the metathesis of acetylenes.[6]

In this paper we report a test of the mechanism that is similar to reaction 2. A mixture (eq 5) consisting of an acy-

(5)
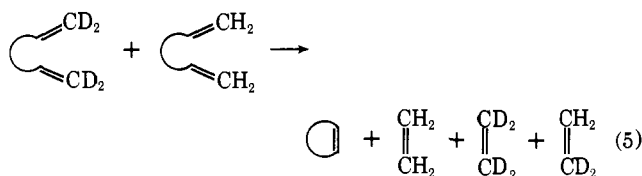
clic diene isotopically labeled at both ends (say with terminal CD_2 groups) and of the same diene unlabeled is subjected to metathesis. According to the conventional mechanism, the dideuterated ethylene should not be an initial product as long as the metathesis of olefins that are connected is faster than that of two ethylenes that are unconnected and as long as the metathesis reaction (step 1 in eq 4) is rate determining. According to the chain mechanism illustrated in Scheme I, the tetra-, di-, and undeuterated ethylenes should

Scheme I
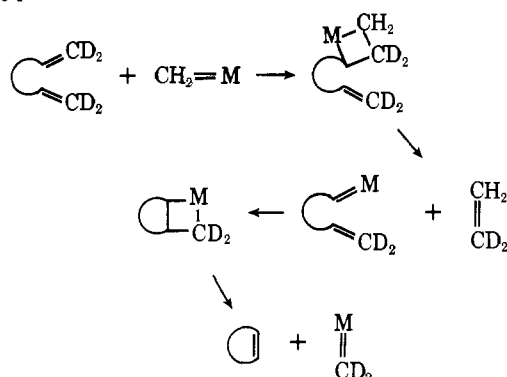
form in 1:2:1 ratio if the deuteriums serve only as labels. Thus, the initially predominant product according to one mechanism should not initially be a product at all according to the other. In the discussion section, we consider what the expected consequences would be if the conventional mechanism were correct, but the olefin-displacement reaction (step 2 in eq 4) were rate determining.

In order for the metathesis to give a cycloalkene, the diene should be chosen so that the two double bonds are separated by four carbons, because while 1,7-octadiene upon metathesis gives cyclohexene and ethylene,[2b,3] 1,5-hexadiene gives linear polyolefins and no cyclobutene[2b,3c]

and because among simple unsubstituted cycloolefins, only cyclohexene undergoes no metathesis.[19] The experiment should therefore be performed with 1,7-octadiene itself or a derivative. The first version of the experiment tried in our laboratory was the metathesis of octa-1,7-diene-$1,1$-d_2 (IV) to see whether undeuterated and tetradeuterated ethylene would form. However, the experiment required mass spectrometric analysis of the diene, for which fragmentation of carbon-hydrogen bonds in the mass spectrometer must be suppressed,[20] and as we could not suppress this fragmentation using IV and our mass spectrometers,[21] we instead

Va, R = D
b, R = H
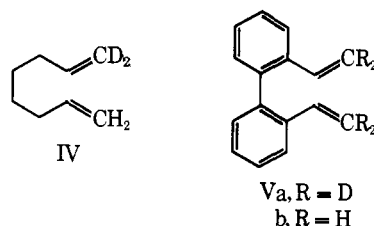
turned to the version of the experiment we are reporting here, in which the metathesis is effected with a mixture of equal amounts of divinylbiphenyl-d_4 (Va) and undeuterated divinylbiphenyl (Vb),[22] and the test is to see whether ethylene-d_0, -d_2, and -d_4 form in ratios 1:0:1 or 1:2:1.

Results

The experiment was performed as follows. Tetradeuterated divinylbiphenyl (Va, 0.050 mmol) and an equal quantity of undeuterated divinylbiphenyl (Vb, 0.050 mmol) were combined in 1 ml of hexane. The mixture was prepared in a dry 1-dram vial, flushed with nitrogen, and capped with a rubber septum. Three μmol of the molybdenum or tungsten catalysts described below were added in hexane solution (ca. 0.05 M), followed by 13-27 μmol of methylaluminum sesquichloride [$(CH_3)_3Al_2Cl_3$] in a mixture of heptane and hexane.[23] The solution, now about 1.2 ml in volume, was shaken vigorously for 30 s, which as shown below allows only small conversion to product, and reaction was then terminated by the addition of 1 ml of absolute ethanol. Samples (ca. 1.5 ml) of the gas above the reaction mixture were removed by syringe and analyzed for the ratios of dideuterated, undeuterated, and tetradeuterated ethylenes. The analyses are in Table I.

The ratios of the d_0, d_2, and d_4 ethylenes produced are about 1:2:1, much different from the 1:0:1 ratio of the d_0, d_2, and d_4 divinylbiphenyls from which they are formed. The difference cannot be attributed to rapid scrambling of d_0, d_2, and d_4 divinylbiphenyls before appreciable amounts of ethylene begin to evolve because divinylbiphenyl recovered from the reaction mixtures was found by mass spectrometry to still consist of undeuterated and tetradeuterated materials in approximately equal amount, with no appreciable additional dideuterated material. The data are also in Table I.

The disparity can also not be ascribed to rapid scrambling of the ethylenes to 1:2:1 ratios after they are initially formed but before they are analyzed by mass spectrometry because metathesis of undeuterated divinylbiphenyl in the presence of trans-1,2-dideuterioethylene does not give appreciable amounts of $CHD\!=\!CH_2$. The experiment was conducted in the same way as that above, but with an amount of $CHD\!=\!CHD$ added that was chosen to be comparable with the amount of C_2H_4 that would be produced. If scrambling had occurred, $CHD\!=\!CH_2$ should have been detected mass spectrometrically as a peak at m/e 29. However, the ratio of the intensity of this peak and the peak at m/e 28 due to $CH_2\!=\!CH_2$ (after minor correction for the peak at m/e 28 produced by the $CHD\!=\!CHD$ sample

Table I. Composition of Ethylenes Evolved after Short[a] Metathesis of a Mixture of Va and Vb, and Percent Scrambling in the Recovered Divinylbiphenyl

| | Sample no. | | | | | | | Av | Std dev |
	1[c]	2	3	4	5	6	7		
Components, μmol									
Va	25	50	50	50	50	50	25		
Vb	25	50	50	50	50	50	25		
Mo[d]	1.35	2.7	2.7	2.7					
W[d]					2.7	2.7	1.35		
MASC[d]	13.5	27	27	27	13.5	13.5	6.8		
Ethylene formed, %									
d_0	28.09	24.07	24.17 23.97	24.51 23.95 25.13	24.45 23.79	23.75 21.58 24.20		24.3	1.5
d_2	48.56	49.74	47.15 48.13	48.79 49.78 51.06	50.12 50.15	49.65 42.27 49.14		48.7	2.3
d_4	23.35	26.19	28.68 27.90	26.70 26.28 23.81	25.42 26.05	26.61 22.54 26.66		25.9	1.8
% scrambling[b] in recovered divinylbiphenyl			1.4	1.1	0.4	2.0	1.1		

[a] The reaction time was 30 s, except for sample 2, for which it was 34 s. [b] The "percent scrambling" is one-half the excess of dideuterated divinylbiphenyl present in the recovered divinylbiphenyl (above that present in the starting hydrocarbon mixture) divided by the amount of undeuterated divinylbiphenyl. [c] Only half as much solvent was used in this experiment. [d] Mo, Mo catalyst; W, W catalyst; MASC, methylaluminum sesquichloride.

alone) was only 3%, as is shown in Table II. Thus, scrambling among ethylenes can also not account for the ratios in Table I.

For the experiments described in Table II, the *trans*-$CHD=CHD$ used was analyzed mass spectrometrically to contain at most 0.6% as much $CH_2=CH_2$ and 7.7% as much $CH_2=CHD$ as $C_2H_2D_2$. The responses of both the mass spectrometer and the gas chromatograph suggest that about 90–95% of the ethylene in the reaction vessel is in solution and only 5–10% in the gas phase. Because of this and because the reaction vessels were also shaken vigorously both before and after the catalysts were added, we believe the failure of the $CHD=CHD$ and $CH_2=CH_2$ to scramble cannot be attributed to their not mixing physically.

The experiment in Table II also indicates the fraction of the divinylbiphenyl that is converted under the reaction conditions into ethylene. Assuming none of the dideuterated ethylene is lost during the experiment, the mass spectrometrically determined ratio of C_2H_4 to $C_2H_2D_2$ in the product when multiplied by the amount of $C_2H_2D_2$ in the original reaction mixture shows the amount of C_2H_4 formed. When divided by the amount of divinylbiphenyl used, it indicates (see Table II) the conversion to ethylene under the reaction conditions to be about 1%. This is similar to the ratio of phenanthrene to divinylbiphenyl in the recovered material, measured approximately by gas chromatography as 2% for samples 3–7 in Table I.

The analysis of the ethylenes was accomplished by an instrument system consisting of a gas chromatograph, a mass spectrometer,[24] and an electronic data acquisition system coupled in tandem. The instruments were the Finnigan[25] Model 3300 gas chromatograph–mass spectrometer with Finnigan's Model 6000 computer. The gas chromatographic column, packed with Porapak Q,[26,27] separated ethylene from oxygen and nitrogen, which would have interfered with the mass spectrometric analysis because O_2 and C_2D_4 have the same molecular weights as do N_2 and C_2H_4. The gas chromatographic column, however, also effects partial separation of the deuterated ethylenes[28] and, in our system, resulted in the maximum for the C_2D_4 peak appearing 5 s before that for C_2H_4 when the ethylene retention time was 7 min. This means that any single mass spectrum of the effluent from the gas chromatograph does not show what the isotopic composition is of the ethylenes injected into the gas chromatograph. However, by measuring the spectrum quickly and storing it in a computer, the Finnigan spectrometer could acquire 250–350 spectra during the time the

Table II. Amount $CHD=CH_2$ Formed as a Percentage of $CH_2=CH_2$ Formed after Short Metathesis (30 s) in the Presence of $CHD=CHD$ Percent Conversion of Vb to Ethylene

	Sample no. 8	9	10	11
Components (μmol)[a]				
Vb	50	50	50	50
$CHD=CHD$	3.1	1.2	3.1	1.2
Mo[b]	1.4	1.4		
W[b]			1.4	1.4
MASC[b]	27	27	14	14
Amount $CHD=CH_2$ as % $CH_2=CH_2$	2.8	3.7	1.8	3.2
Percent reaction = amount $CH_2=CH_2$ as % Vb[c]	1.2	1.1	1.5	0.8

[a] Also about 0.6 ml of hexane + heptane as solvent. [b] Mo, Mo-catalyst; W, W-catalyst; MASC, methylaluminum sesquichloride. [c] The amount of $CH_2=CH_2$ is the mass spectrometrically measured ratio $[CH_2=CH_2]/[CHD=CHD]$ times the amount of $CHD=CHD$ added to the original reaction mixture.

ethylenes eluted. The sum of the intensities for each mass peak (corrected for background) was then used as the measure of the concentration of the individual ethylenes.

The Finnigan spectrometer measures the spectra quickly by using a quadrupole mass filter[29] to focus the ions. We adjusted the instrument to measure the intensity of each peak in 20 ms, and the seven peaks at m/e 27–33 were, thus, measured in 0.14 s. For the analysis in Table II, the mass spectrometer was operated in its "multiple ion detection mode",[30] which consumed more time, and only 40–50 mass spectra were acquired during the time the ethylenes eluted.

The analysis of the deuterium content of the divinylbiphenyl samples was accomplished by observing the intensities of the alkylated ions formed by addition of $C_2H_5^+$ to the parent molecule upon methane chemical ionization mass spectrometry.[32] The use of the chemical ionization spectrum was significant because all attempts to minimize the ratio of the fragment peak of mass M − 1 to that of the parent ion at mass M in electron impact mass spectra never gave us ratios smaller than 20%, making accurate analysis of deuterium content impossible.[21] In the chemical ionization mass spectrum, however, undeuterated divinylbiphenyl showed peaks at m/e 237 and 239 that were only 2.5 and 1.4% as intense as the peak corresponding to M + $C_2H_5^+$, at m/e 235; tetradeuterated divinylbiphenyl showed corresponding peaks at m/e 237 and 235, which were only 2.0 and 1.4% as intense as the peak at m/e 239. Thus, to analyze the amount of scrambling in recovered divinylbiphenyl,

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as summarized in Table I, only small corrections had to be applied to the mass spectrometric data to allow for the contributions of undeuterated material to the peaks at 237 and 239 and of tetradeuterated material to the peaks at 235 and 237.

The methane chemical ionization mass spectrum of the tetradeuterated divinylbiphenyl should also show the fraction of the nominally tetradeuterated material containing 0, 1, 2, and 3 deuteriums. However, a more accurate analysis could be achieved by conducting a tungsten-catalyzed metathesis and analyzing the ethylene produced. This indicated the material to be 96.4% tetradeuterated, and 2.3% tri-, 0.5% di-, 0.1% mono-, and 1.0% undeuterated. The essential result is that the fraction of the methylene groups that are dideuterated is greater than 98%.

The molybdenum and tungsten portions of the catalyst system were prepared by combining $Mo(CO)_6$ or $W(CO)_6$ with NOCl and then with tri-n-octylphosphine, a sequence patterned on the preparations of $M[(C_6H_5)_3P]_2(NO)_2Cl_2$, $M = Mo$, and W,[32] materials which with methylaluminum sesquichloride are active metathesis catalysts.[2b] Tri-n-octylphosphine was substituted for triphenylphosphine with the thought that the resulting material would be more soluble in alkane solvents, and, while this proved true, the products were brown viscous oils that could not be crystallized. However, as they exhibited good catalytic activity, they were used for the experiments. Control experiments, in which methylaluminum sesquichloride was combined with the molybdenum and tungsten catalysts exactly as in the metathesis experiments but without divinylbiphenyl, showed that less than 3%[34] as much ethylene was formed as when the divinylbiphenyl was present.

Discussion

The observation that a 1:0:1 mixture of d_0, d_2, and d_4 divinylbiphenyls gives a 1:2:1 mixture of d_0, d_2, and d_4 ethylenes is not in accord with the conventional mechanism if the metathesis reaction, step 1 of eq 4, is rate determining. This mechanistic possibility is therefore excluded.

The observation is, however, in accord with the mechanism of eq 1. Thus, if the rates of the four reactions 6 are $k_R k_{R'}[R_2C{=}M][O_{R'}]$,

$$R_2C{=}M + \quad \longrightarrow \quad + R_2C{=}CR'_2 \quad (6)$$
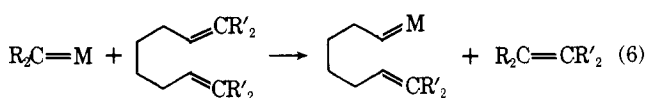
where R can be H or D, R' can be H or D, and $O_{R'}$ represents diene substituted by R', at the steady state

$$\frac{[H_2C{=}M]}{[D_2C{=}M]} = \frac{k_D k_{H'}[O_H]}{k_H k_{D'}[O_D]}$$

Suppose $k_H/k_D = k_{H'}/k_{D'} = r$, the isotope effect. If we symbolize $[O_H]/[O_D]$ as y, then the ratios of the rates of formation of d_0, d_2, and d_4 ethylenes are $r^2y^2{:}2ry{:}1$. When $y = 1$, as in the experiment described, the ratios should be $r^2{:}2r{:}1$, and when the isotope effect r is unity, 1:2:1. The isotope effect is considered further, below.

Consider a third possibility, that the conventional mechanism is correct, but step 2 of eq 4 is rate determining. There are six possible reaction sequences as shown in Scheme II. Suppose the rate constants for all reactions that attach to the metal olefins with hydrogens are r times the rate constants for the corresponding reactions that attach to the metal olefins in which two hydrogens are replaced by deuteriums. (We suppose the ratio to be the same in the first and second steps.) Call the ethylene complex with n deuteriums, C_n, and diene with n deuteriums, O_n, and the ratio $[O_0]/$

Scheme II
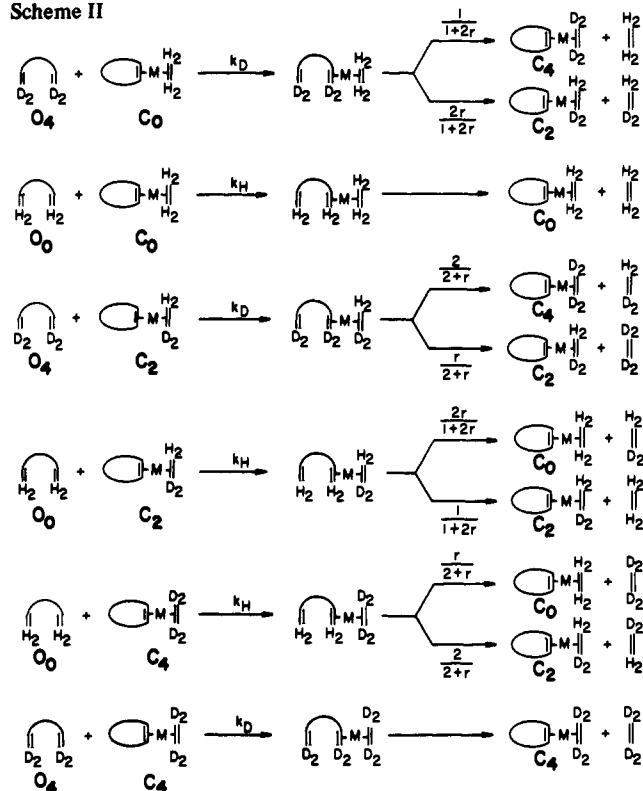
$[O_4]$, as above, y. We assume the two ends of the ethylene when bonded to the metal react equivalently.[35] Then at the steady state, eq 7 applies.

$$\begin{bmatrix} \dfrac{1}{1+2r} & -ry \\[2ex] -1 & \dfrac{r^2y}{r+2} \end{bmatrix} \begin{bmatrix} [C_0] \\[2ex] [C_4] \end{bmatrix} = [C_2] \begin{bmatrix} \dfrac{-2}{2+r} \\[2ex] \dfrac{-2r^2y}{1+2r} \end{bmatrix} \quad (7)$$

The rates of formation of the three ethylenes are given by eq 8-10.

$$\frac{d[C_2H_4]}{dt} = \frac{k_D}{1+2r}[O_4][C_0] + k_H[O_0][C_0] + \frac{k_H}{1+2r}[O_0][C_2] \quad (8)$$

$$\frac{d[C_2H_2D_2]}{dt} = \frac{2rk_D}{1+2r}[O_4][C_0] + \frac{2k_D}{2+r}[O_4][C_2] + \frac{2rk_H}{1+2r}[O_0][C_2] + \frac{2k_H}{2+r}[O_0][C_4] \quad (9)$$

$$\frac{d[C_2D_4]}{dt} = \frac{rk_D}{2+r}[O_4][C_2] + \frac{rk_H}{2+r}[O_0][C_4] + k_D[O_4][C_4] \quad (10)$$

Applying eq 7 then gives the ratios of the rates of formation of the three ethylenes as functions of the isotopic composition of the diene substrate and of isotope effect r.

Suppose $y = 1$, as in the experiment described, and suppose $r = 1$. Equation 7 shows then that $[C_0] = [C_2] = [C_4]$, a consequence of the equal probability for the different deuterated complexes to form on the right side of Scheme II.

The ratio of the rates of formation of the d_0, d_2, and d_4 ethylenes under these conditions is calculated to be 1:8/5:1. The 8/5 can be seen in Scheme II as the ratio of the probabilities of forming the d_2 ethylene and either the d_0 or d_4 ethylene under the supposition, proven above, that the C_0, C_2, and C_4 complexes are present in equal amounts.[35]

Table III. Dependence of the Ratios of the Rates of Formation of Ethylene-d_0, -d_2, and -d_4 on the Isotope Effect r Assuming the Applicability of Scheme II[a]

| r	$d[C_2H_2D_2]/$ $d[C_2H_4]$	$d[C_2D_4]/$ $d[C_2H_4]$	$d[C_2H_2D_2]/d[C_2H_4]$ $\times d[C_2H_2D_2]/d[C_2D_4]$
0.75	2.07	1.68	2.56
0.80	1.95	1.49	2.56
0.85	1.85	1.34	2.56
0.90	1.76	1.21	2.56
0.95	1.68	1.10	2.56
1.00	1.60	1.00	2.56

[a] The ratio $y = [O_0]/[O_4]$ is assumed to be 1.

The dependence of the product ratios on r is indicated in Table III.[36] There is only one set of measurements we could find of the isotope effect on the stability constants of deuterated olefin–metal complexes. For 1,1-dideuteriopropylene–Ag$^+$, the stability constant is 1.06 times that for undeuterated propylene.[37,38] This would suggest that r be chosen as 0.94, but the evidence is not large, and other choices seem possible. However, the observed ratios recorded in Table I do not appear in accord with any of the calculated ratios in Table III, no matter what isotope effect is chosen. The best way to see this is to consider the product of the ratios $d[C_2D_2H_2]/d[C_2H_4]$ and $d[C_2D_2H_2]/d[C_2D_4]$. As can be seen in Table III, this product is calculated to be 2.56 [essentially $(8/5)^2$],[39] independent of the actual isotope effect.

According to the carbene chain mechanism, eq 1, the ratios of the rates of formation of the d_0, d_2, and d_4 ethylenes, as indicated above, should be $r^2:2r:1$, and the product $d[C_2D_2H_2]/d[C_2H_4] \times d[C_2D_2H_2]/d[C_2D_4]$ should therefore be $(2r/r^2)(2r/1) = 4$, independent of r. The measured product using the data in Table I is (% $d_2)^2/($% $d_0)($% $d_4)$ = 3.80 ± 0.31. According to the t test,[40] the mean of 12 experimental measurements whose standard deviation is 0.31 would be expected to differ from 4 by 0.2 in 95% of statistical samplings, but to differ from 2.56 by 1.24 in fewer than one sampling in ten million.[40b] Thus, the measurements are in accord with the mechanism of eq 1 and essentially inconsistent with the mechanism of eq 4, even if the second step were rate determining.

There is also an experimental virtue to using the product $d[C_2D_2H_2]/d[C_2H_4] \times d[C_2D_2H_2]/d[C_2D_4]$ to test the mechanism. That is, there might have been an isotope effect that fractionated the ethylenes in the course of their analysis, most notably in the gas separator, between the gas chromatograph and the mass spectrometer, which in removing much of the helium from the gas stream would also remove more of the less deuterated ethylene than the more deuterated material. The product of the ratios used to test the mechanism should correct experimental error introduced in this way.

Mechanisms can also be imagined that are similar to Scheme II, but in which the metals are always bonded to three olefins, to two ethylenes, and to one other, for example, as in structure VI. There would now be five complexes

VI
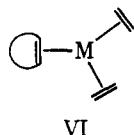
C_{2m} ($m = 0, 1, \ldots, 4$) rather than three, and assuming $y = 1$ and $r = 1$, as above, at the steady state their concentrations should be in the ratios $[C_0]/[C_4] = [C_8]/[C_4] = 17/42$ and $[C_2]/[C_4] = [C_6]/[C_4] = 32/42$. The ratios of the rates of formation of the monodeuterated and either the

di- or the undeuterated ethylene should be 32/19, and this squared is 2.84. The details are in the Appendix. Again, according to the t test applied as above, the likelihood that the experimental product ratios in Table I would differ so much from the expected ratios is less than 2.5 in ten million. Accordingly, this mechanism is rejected.

The experiment described here and the experiment indicated in eq 2 are closely related. The differences are that the one experiment is essentially the reverse of the other and that the labels in the one are different alkyl groups, while in the other different isotopes.

The rigor with which either experiment proves the mechanism depends on the strengths of the arguments that can be brought to bear against the idea that the initial reaction in either experiment is a polymerization, followed by a depolymerization. If the ethylene were formed in the experiments recorded here by two dienes reacting intermolecularly, the ratios of the d_0, d_2, and d_4 ethylenes would be 1:2:1, no matter what the mechanism. The phenanthrene, it would have to be supposed, is formed subsequently. The argument we offer to counter this supposition is that an intermolecular reaction competing with an intramolecular cyclization giving a six-membered ring seems improbable, especially as some kind of an intramolecular reaction giving phenanthrene must occur at about the same rate as ethylene is evolved. That it is the same reaction that makes or breaks the ring that also gives the scrambled product seems clearer, however, for the scheme in eq 2, although there is an argument similar to the one above that must be countered.[41]

Another advantage of the experiment in eq 2 is that because the labels are different alkyl groups, the analysis could be effected by gas chromatography, rather than by the more difficult mass spectrometry. The advantage of the experiment described here is that the greater theoretical understanding of the effects upon reactions of substituting deuterium for hydrogen rather than one alkyl group for another must make the substituent, or isotope, effect as measured by r be in the range covered in Table III.

The experiments reported here thus seem to prove that the mechanism of the olefin metathesis reaction does not involve the union of two olefin molecules as has been supposed, but involves the carbene chain mechanism in eq 1.

Experimental Section

Abbreviations. The following abbreviations are used: MS, mass spectrometry; EI, electron impact; CI, chemical ionization; GC, gas chromatography; PMR, proton nuclear magnetic resonance; MASC, methylaluminum sesquichloride [$(CH_3)_3Al_2Cl_3$].

2,2′-Divinylbiphenyl. This material was prepared from 2,2′-bis-(triphenylphosphoniomethyl)biphenyl dibromide[42] following the procedure of Staab et al.[43] After chromatography on silica gel (hexane eluent) and recrystallization from hexane, the melting point was 76.5–81.5 °C (reported[42] 78–79 °C).

2,2′-Di(β,β'-dideuterio)vinylbiphenyl. This was prepared as above, but using Merck paraformaldehyde-d_2, stated to be of 98% minimum isotopic purity. The product after chromatography was treated in hexane with methyl iodide to remove residual triphenylphosphine. Filtration, removal of some solvent, and crystallization gave the product, mp 78.5–80 °C. The PMR spectrum showed no trace of the resonances due to the CH$_2$= protons of Vb, at δ 5.56 and 5.03.

The methane chemical ionization mass spectra of undeuterated and tetradeuterated divinylbiphenyls in the mass range 233–241 are presented in Table IV.

The ethylene formed by metathesis of 50 μmol of the deuterated material, with 1.35 μmol of the tungsten compound and 13.6 μmol of methylaluminum sesquichloride in 0.6 ml of hexane-heptane for 60 s, on EI-GC-MS showed peaks from mass 33 down to 27 of intensities 1.66, 100, 2.36, 1.67, 0.07, 2.74, 0.11, while C$_2$H$_4$ similar-

Table IV. Methane Chemical Ionization Spectra of Divinylbiphenyls

m/e	Undeuterated	Tetradeuterated
233	1.60	0.17
234	2.12	0.29
235	100	1.37
236	20.31	0.38
237	2.54	1.95
238	0.39	3.58
239	1.39	100
240	0.48	22.47
241	0.70	2.56

ly formed from undeuterated divinylbiphenyl showed peaks from mass 29 to 26 of intensities 2.39, 100, 0.81, 1.25.

Mo and W Complexes. $Mo(NO)_2Cl_2$ was prepared from 3.04 g of $Mo(CO)_6$ as described by Cotton and Johnson.[32] After removing the solvent with an aspirator, the product, still in the flask in which it was made, was combined with benzene (16 ml) and then tri-n-octylphosphine (8.50 g) in 10 ml of benzene (exothermic), whereupon it dissolved. After the mixture was stirred for 10 min, refluxed for 1 h, and stirred at ambient temperature for another 2⅔ h, the solvent was alternately vaporized into an aspirator and replenished with 40-ml portions of petroleum ether (30-60 °C). Removal of the solvent left 11.1 g of a brown–black viscous oil that was used without purification. The tungsten analogue, made similarly, was a somewhat less viscous and lighter colored oil. A few attempts to purify these materials by crystallization or chromatography were unsuccessful.

An assumption in measuring them was that their formulas are $M(NO)_2Cl_2[P(octyl)_3]_2$, M = Mo and W, analogous to the known materials prepared from triphenylphosphine.[32]

trans-**Dideuterioethylene.** Dideuterated acetylene[44] was reduced in the absence of air according to the procedure of Nicholas and Carroll[44a] and deoxygenated over pyrogallol in concentrated aqueous KOH. GC at 61 °C using a 2 m × ⅛ in. o.d. column packed with 100/120 mesh Porapak N[45] showed that less than one part per thousand of acetylene remained. The EI–MS showed peaks at masses 31 through 28 with the following intensities: 2.09, 100, 7.67, 0.59.

Ethylenes from Metathesis of Va plus Vb. Fisher spectroscopic grade "hexanes" were washed with concentrated H_2SO_4, H_2O, and aqueous Na_2CO_3 and then dried and distilled onto 4A molecular sieves. Methylaluminum sesquichloride, obtained from Texas Alkyls, Inc., as a 25% (w/w) solution in heptane and found by titration to be 0.80 M, was either used directly or diluted with hexane. The W and Mo compounds were dissolved in hexane.

A 1-dram vial was dried at 110 °C, capped with a rubber septum, and cooled while passing nitrogen in through one syringe needle and out a second. The needles were removed, and divinylbiphenyl (typically 0.5 ml, 0.1 M in hexanes, 0.05 mmol) was syringed in, followed by the required amounts of the Mo or W catalyst solutions. MASC solution was then added, the stopwatch was started, and the vial was vigorously shaken by hand until the reaction was terminated by injecting 1.00 ml of absolute ethanol.

The evolution of ethylenes was recognized by GC analysis of 100-μl headspace aliquots using a 2 m × ⅛ in. o.d. 100/120 Porapak Q column[26,27] at temperatures of about 22-45 °C. The only components detectable by the flame-ionization detector were methane (from MASC ethanolysis), ethylene, and ethane (from ethanolysis of an impurity in MASC), with approximate retention times of 1, 3, and 4 min, respectively. [Other components expected (hexanes, ethanol, heptane, etc.) have extremely long retention times on Porapak Q near ambient temperature.] By comparing the ethylene peak heights in metathesis samples and in pure ethylene, the amount of the ethylenes in a 100-μl headspace sample was estimated as about 0.1 μl, about 0.005 μmol or 0.1 μg.

For GC–MS analysis of the ethylenes, a 6 m × ⅛ in. o.d. 100/120 Porapak Q column[26,27] was employed, and He was the carrier gas. Larger quantities of ethylene were required, and a 2-ml syringe with a syringe stopcock was used to withdraw samples. The headspace in the sample was under sufficient pressure from the metathesis reaction to expand about 1 ml into the syringe. By pulling back the plunger and closing the syringe stopcock, about 1.5 ml of headspace was withdrawn. This was estimated to contain ~1 μl

of ethylene by comparing the mass spectrometer's response with its response to samples of pure ethylene. Samples for repeat injections were obtained by first warming samples to ~40 °C and injecting ~2 ml of air, moving the syringe plunger in and out a few times to mix evolved ethylenes in the headspace, and then closing the syringe stopcock. These repeat injections contained less than half as much ethylenes as did the first injections.

The mass spectrometry was performed as follows. The energy of the bombarding electrons was decreased until the peak at m/e 26 displayed by a sample of C_2H_4 was less than 1% as intense as that at m/e 28.[46] To minimize destruction of the filament by air, the filament current was not turned on until 45 s before the maximum in ethylene eluent was anticipated. At the same time, computer acquisition of mass spectroscopic data was begun and continued until somewhat after the intensities, viewed on a cathode ray tube (CRT), of the peaks at m/e 27 through 33 returned to background levels. About 250-350 spectra were acquired while the ethylenes eluted, the integration time of the mass spectrometer having been fixed at 20 ms/peak. To measure intensities, the data for one m/e value was recalled from the computer and displayed on the CRT. The scans corresponding to beginning and end of the peak were determined. The 10 consecutive scans just before the peak measured the "prior background" and the 10 consecutive scans just after the peak determined the "post-peak background". The computer established a baseline under the peak using these 20 scans and the least-squares algorithm for a straight line. The computer summed the intensities above the background, correcting thereby for any residual N_2 and O_2.[46] The procedure was then repeated for other values of m/e. The CRT displays of intensities vs. scan number for all m/e values showed no flat tops, which would have invalidated the data. The results are presented below in Table V and summarized in Table I.

Recovery of Divinylbiphenyl from Metathesis Reactions. Divinylbiphenyl was recovered from the samples of Va + Vb subjected above to metathesis. Solvent was evaporated under a nitrogen stream, and the residue was triturated with about 1 ml of chloroform. The extract when applied to a silica gel preparative layer chromatography plate (1-mm thickness, 20 × 20 cm, with fluorescent indicator, Analtech) and developed with spectral hexanes showed one major mobile band (R_f 0.27) under ultraviolet light, and this was scraped off and extracted in a sintered glass funnel with 12 10-ml portions of chloroform. The combined filtrates were concentrated to a crude residue that was examined by proton NMR to confirm the presence of the mixed divinylbiphenyls.

The amount the CH_2 groups scrambled between molecules of divinylbiphenyl was analyzed by methane chemical ionization mass spectrometry. The data are in Table VI and summarized in Table I. The percent scrambling is one-half of

$$I_{237} - \frac{1.95(I_{239} - 1.39)}{100} - \frac{2.54}{100}\left[I_{235} - \frac{1.37(I_{239} - 1.39)}{100}\right]$$

where I_{235}, I_{237}, and I_{239} are the relative intensities of the peaks at m/e 235, 237, and 239. The numbers 1.95, 1.39, and 2.54 are from Table IV, the mass spectra of the undeuterated and tetradeuterated divinylbiphenyls. The one-half accounts for one reaction between d_0 and d_4 divinylbiphenyls giving two molecules of divinylbiphenyl-d_2.

By using GC on 5 ft × ⅛ in. o.d. 20% Apiezon L on 100/120 Chromosorb W Regular at 255 °C, phenanthrene was found in the samples of divinylbiphenyl recovered above by thin layer chromatography. The areas of the peaks due to phenanthrene as a percent of the areas of the peaks due to divinylbiphenyl are for samples 3-7, 2.2, 0.7, 2.7, 3.2, and 2.5%. The samples may have been fractionated on chromatography, and these numbers therefore only indicate that phenanthrene is formed to the extent of one or a few percent.

Ethylenes from Metathesis of Vb in the Presence of CHD=CHD. The procedure was the same as above, except that 15 to 75 μl of CHD=CHD was injected into the sample vial, which was then shaken vigorously for 15 s, before the Mo, W, or MASC

Table V. Intensities of Mass Spectrometric Peaks of Ethylene Samples from Metathesis of Va + Vb[a]

m/e	Sample no.[b]										
	1	2	3		4			5		6		
28	59.79	50.45	53.38	51.91	52.29	50.16	51.19	50.80	49.48	49.89	54.40	53.09
29	2.36	3.41	3.52	2.99	2.13	3.70	3.43	2.96	2.90	2.04	3.24	3.05
30	100	100	100	100	100	100	100	100	100	100	100	100
31	2.59	3.76	3.58	3.31	2.98	3.71	2.63	3.66	3.35	3.00	3.24	2.07
32	47.82	52.33	60.41	57.60	54.38	52.47	46.38	50.43	51.64	53.27	38.84	53.32

[a] For ethylene itself the relative intensities of the peaks at m/e 28, 27, and 26 were 100:0.96:1.17. [b] The sample numbers are the same as in Table I.

Table VI. Methane Chemical Ionization Mass Spectra of Recovered Divinylbiphenyls

Sample no.	3	4	5	6	7
m/e 235	100	100	100	100	100
237	7.59	6.61	5.34	8.46	6.60
239	118.97	101.91	104.31	100.99	97.51

Table VII. Mass Spectrometric Peak Intensities of Ethylenes From Vb + CHD=CHD

Sample no.	8	9	10	11
m/e 28	18.67	44.65	24.07	33.33
29	8.58	10.28	8.60	9.44
30	100	100	100	100

solutions were added. The mass spectrometer was operated in its "multiple ion detection" mode, which resulted in only 40–50 spectra being accumulated during the time the ethylenes eluted. The data are presented in Table VII and summarized in Table II. The amount of CHD=CHD formed, expressed as a percent of the ethylene formed, is

$$\frac{100\left[I_{29} - 7.67 - 0.022(I_{28} - 0.59)\right]}{I_{28} - 0.59}$$

where I_{28} and I_{29} are the intensities of the peaks at m/e 28 and 29 relative to m/e 30 taken as 100. The 7.67 and 0.59 are intensities in the spectrum of the CHD=CHD (see above), and 0.022 is twice the fraction of carbon containing ^{13}C.

Appendix

We consider here a generalized Scheme II, in which the metals are bonded to $N + 1$ olefins, N ethylenes, and one other. The cases considered above, in which $N = 1$ and $N = 2$, are special instances of this general scheme. Suppose the isotope effects are all unity. The steady-state conditions are

$$0 = \left(\frac{2N+1}{2N-1}\right)\frac{d[C_{2m}]}{k dt} = \sum_{s=0}^{1}\sum_{r=0}^{2N}[C_{2r}][O_{4s}]\binom{r+s}{m-s} \times$$

$$\binom{2N+1-(r+s)}{2N-1-(m-s)} - \sum_{s=0}^{1}[C_{2m}][O_{4s}]\binom{2N+1}{2N-1}$$

$$m = 0, 1, \ldots, 2N$$

The rates of formation of $(CH_2)_g(CD_2)_{2-g}$ are proportional to R_g, where

$$R_g = \sum_{s=0}^{1}\sum_{r=0}^{2N}[C_{2r}][O_{4s}]\binom{r+s}{g}\binom{2N+1-(r+s)}{2-g}$$

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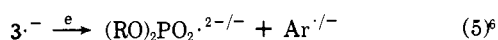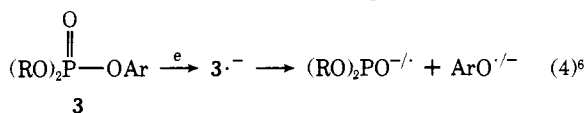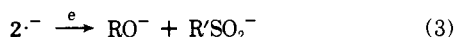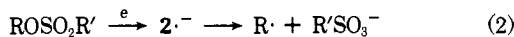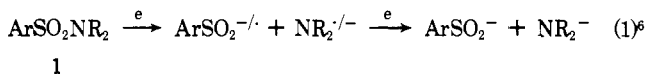# On the Mechanism of Cleavage of Aryl Alkanesulfonates by Electron Donors[1]

J. C. Carnahan, Jr., W. D. Closson,* J. R. Ganson, D. A. Juckett, and K. S. Quaal

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Abstract: In the cleavage of methane- and ethanesulfonates of phenols with arene anion radicals, 2 mol of the reducing species is consumed rapidly, resulting in formation of phenoxide and sulfinate ions. The mechanism involves initial rapid transfer of an electron from donor to sulfonate, followed by a considerably slower cleavage step. The effect of substituents on both these steps has been determined. With donors of higher reducing power, C–O cleavage yielding arene becomes more important. Tentative explanations for this latter effect are given.

Introduction

In our studies of the reaction of sulfonyl derivatives with electron donors we have discovered two rather different types of mechanisms of cleavage. With arenesulfonamides (1) the initial electron-transfer step is rate controlling and results in S–N cleavage exclusively.[2] This is followed by rapid further reduction resulting in formation of sulfinate and amide anions (eq 1).[3] With alkyl alkanesulfonates (2)

$$ArSO_2NR_2 \xrightarrow{e} ArSO_2^{-/\cdot} + NR_2^{\cdot/-} \xrightarrow{e} ArSO_2^- + NR_2^- \quad (1)^6$$

1

$$ROSO_2R' \xrightarrow{e} 2^{\cdot -} \longrightarrow R\cdot + R'SO_3^- \quad (2)$$

2

$$2^{\cdot -} \xrightarrow{e} RO^- + R'SO_2^- \quad (3)$$

$$(RO)_2\overset{\overset{O}{\parallel}}{P}-OAr \xrightarrow{e} 3^{\cdot -} \longrightarrow (RO)_2PO^{-/\cdot} + ArO^{\cdot/-} \quad (4)^6$$

3

$$3^{\cdot -} \xrightarrow{e} (RO)_2PO_2^{\cdot 2-/-} + Ar^{\cdot/-} \quad (5)^6$$

initial electron transfer results in a metastable substrate anion radical ($2^{\cdot -}$) which, if nothing further transpires, undergoes C–O cleavage yielding alkyl radical and sulfonate anion (eq 2).[4] If, however, the concentration and/or reducing power of the electron donor is high enough, another electron is transferred and a different mode of cleavage, S–O, occurs (eq 3).[4] Recently, we have observed a slightly

different version of this latter mechanism in the electron transfer reactions of aryl phosphates (3).[5] Here, the initial substrate anion radical ($3^{\cdot -}$) undergoes P–O cleavage (eq 4), but if further reduced cleaves at the C–O bond (eq 5). In this work we wish to present an example of a sulfonyl derivative system, that of aryl alkanesulfonates (4), which ap-

X—⟨benzene ring⟩—OSO₂CH₃

4
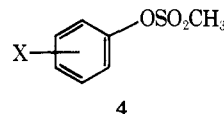
a, X = H	**h**, X = *m*-CF₃
b, X = *m*-CH₃	**i**, X = *p-t*-C₄H₉
c, X = *p*-CH₃	**j**, X = *o*-CH₃
d, X = *m*-OCH₃	**k**, X = *p*-Br
e, X = *p*-OCH₃	**l**, X = *o*-OCH₃
f, X = *m*-Cl	**m**, X = *p*-C₆H₅
g, X = *p*-Cl	

pears to follow the reaction pattern of aryl phosphates. Also, we wish to present information on substituent effects on different steps of the reaction. Finally, we would like to propose explanations for the differences in behavior of these different classes of compounds on reductive cleavage.

Results and Discussion

Treatment of THF or DME solutions of aryl methanesulfonates with any of a wide variety of arene anion radicals results in rapid disappearance of the anion radical and formation of aryloxide and methanesulfinate ion in nearly