samples. The independent synthesis of indene **15** is given below.

Run 2. Pyrolysis of 57.4 mg (0.232 mmol) of 1-*tert*-butyl-3-phenylindene (**4**) gave 57.3 mg (100% mass balance) of indene **4** (74%) and indene **15** (26%) in a ratio of 2.8:1.0, respectively, by ^{1}H NMR. GC retention times were matched against authentic samples.

Run 3 (Control). Pyrolysis of 50.0 mg (0.202 mmol) of 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (**1**) gave 49.2 mg (98.4%) of recovered allene **1**; ^{1}H NMR showed the allene as completely unchanged; no detectable conversion to products had occurred.

Run 4 (Control). Pyrolysis of 65.2 mg (0.263 mmol) of 4,4-dimethyl-1,1-diphenyl-2-pentyne (**3**) gave 53.3 mg (81.7%) of recovered alkyne **3**; 6.2 mg (9.5%) of a yellow residue remained behind in the glass boat inside the sample chamber. NMR showed only recovered alkyne and no additional products.

Run 5. Pyrolysis of 59.8 mg (0.241 mmol) of 2-*tert*-butyl-3-phenylindene (**5**) gave 59.8 mg (100% mass balance) of indene **5** (64%) and a product identified as 2-*tert*-butyl-1-phenylidene (**16**, 36%) in a ratio of 1.8:1.0, respectively, by ^{1}H NMR. The spectral data of indene **16** follow: ^{1}H NMR ($CDCl_3$) δ 6.4–7.5 (m, 9 H, arom), 6.30 (d, 1 H, J = 2 Hz, olefinic), 4.50 (d, 1 H, J = 2 Hz, methine), 1.05 (s, 9 H, *tert*-butyl). Indene **16** was also a product of triethylamine catalyzed isomerization[28d] of indene **5**. Thus, a solution of 307 mg (1.24 mmol) of indene **5** and 2.9 mL of triethylamine in 30 mL of dry pyridine was heated to 45 °C for 20 h. ^{1}H NMR indicated 5% conversion to **16**. After a total of 51 h NMR analysis showed 84.8% indene **5** and 15.2% indene **16**. The GC retention times of the indenes in the mixture matched indenes **5** and **16** in the pyrolysis reaction mixture.

Independent Synthesis of 3-*tert*-Butyl-1-phenylindene (15). Indene **15** was prepared from 9.5 mmol of *tert*-butyl magnesium chloride in 50 mL of dry THF by addition of 2.0 g (9.5 mmol) of 3-phenylindanone[56] in 50 mL of THF following the procedure given for 3-*tert*-butyl-1-methylindene.[57] The crude product, obtained by using the literature workup, was chromatographed on a 20 mm × 330 mm silica gel column eluting with hexane. The first 200-mL fraction gave 28.1 mg of indene **15**. A 1.5 g (75%) recovery of 3-phenylindanone was obtained by stripping the column with diethyl ether eluant. The spectral data for indene **15** follow: ^{1}H NMR ($CDCl_3$) δ 7.0–7.7 (m, 9 H, arom), 6.20 (d, 1 H, J = 2 Hz, olefinic), 4.43 (d, 1 H, J = 2 Hz, methine), 1.40 (s, 9 H, *tert*-butyl); IR (CCl_4) 3.21, 3.25, 3.32, 3.42, 6.21, 6.67, 6.83, 7.14, 7.30, 8.03, 8.26, 8.55, 9.22, 9.62, 9.90, 11.30, 11.70, 14.18 μm.

Acid-Catalyzed Rearrangements of 1-*tert*-Butyl-3,3-diphenylcyclopropene (2) and Resemblance to Wall Effects in Pyrolyses. A pyrolysis of 48.8 mg (0.197 mmol) of cyclopropene **2** was run at a much lower temperature, 250 °C (1 mm), than the runs described above. Condensation onto the hot walls of the tube resulting in catalyzed isomerization of cyclopropene **2** seemed likely since the products were those obtained from rearrangement catalyzed by protic acid. After the pyrolysis, 48.8 mg (100% mass balance) of an oil was obtained; ^{1}H NMR analysis showed 60% unreacted cyclopropene **2**, 28% 2-*tert*-butyl-3-phenylindene (**5**), and 12% 1-*tert*-butyl-3-phenylindene (**4**). For comparison a solution of 45.0 mg (0.182 mmol) of cyclopropene **2** and 5.8 mg (0.031 mmol) of *p*-toluenesulfonic acid in 0.5 mL of benzene-d_6 was heated at 68 °C for 2 days (10% conversion to products) and then at 75 °C for 20 h. ^{1}H NMR analysis showed 25% conversion of cyclopropene **2** to indenes **5** and **4** in the ratio 1.5:1.0, respectively.

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Registry No. **1**, 81740-70-7; **1**-d_1, 95191-86-9; **2**, 42842-57-9; **2**-d_1, 95191-92-7; **3**, 95191-85-8; **3**-d_1, 95191-96-1; **4**, 32338-54-8; **4**-d_1, 95191-90-5; **5**, 95191-88-1; **5**-d_1, 95191-91-6; **8**, 57985-60-1; **9**, 53483-12-8; **10**, 38206-36-9; **11**, 95191-89-2; **11**·Na, 81740-71-8; **13**, 42842-76-2; **14**, 95191-93-8; **15**, 95191-94-9; **16**, 95191-95-0; D_2, 7782-39-0; bromoethane, 74-96-4; 3,3-dimethyl-1-butyne, 917-92-0; bromodiphenylmethane, 776-74-9; bromobenzene, 108-86-1; 3-*tert*-butyl-1-indanone, 50438-04-5; 3-*tert*-butyl-1-phenylindan-1-ol, 95191-87-0; ethyl 2-benzyl-2-cyano-3,3-dimethylbutanoate, 57985-59-8; 2,2-dimethyl-5,5-diphenyl-4-penten-3-one, 844-39-3; 4,4-dimethyl-1,1-diphenyl-2-pentyn-1-ol, 1522-15-2; diphenyldiazomethane, 883-40-9; *tert*-butylmagnesium chloride, 677-22-5; 3-phenylindanone, 16618-72-7.

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Mechanism of Solvolysis of 2,2-Dimethylcyclopentyl *p*-Bromobenzenesulfonate

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Abstract: Solvolysis of the title compound in ethanol–water, trifluoroethanol–water, and hexafluoroisopropyl alcohol–water mixtures yields >90% products of methyl migration. The rate of solvolysis relative to the cyclopentyl analogue is 0.19 in 80% ethanol–water, 4.0 in 97% trifluoroethanol–water, and 10.0 in 90% hexafluoroisopropyl alcohol–water. The α-d and β-d_2 rate effects in solvolyis range respectively from 1.19–1.20 to 1.26–1.30. The results are interpreted in terms of a mechanism which involves reversible formation of the tight ion pair followed by rate-determining methyl migration.

An important question in the study of carbonium ion reactions concerns the timing of the bonding changes which are involved in Wagner–Meerwein rearrangements; does the neighboring group migration occur simultaneously with or subsequent to carbonium ion formation? For example, neopentyl sulfonate esters solvolyze with participation by a neighboring methyl group during irreversible ionization,[1,2] whereas pinacolyl (3,3-dimethyl-2-butyl)-sulfonate esters solvolyze with methyl migration after irreversible ionization.[1,3] We now wish to report for the first time an example

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Table I. Products from the Solvolysis of 2,2-Dimethyl-1-deuteriocyclopentyl *p*-Bromobenzenesulfonate at 25 °C[a]

solvent	III	IV	V	VI
80E[b]	5	42	22	31
70E	6	39	20	36
70T	3	56	21	20
97T	6	62	22	10
90H	3	70	21	6

[a] Expressed as a percentage of total product mixture. Determinations were made by using Varian HR-220 spectrometer operating at 33.8 MHz (^{2}H NMR). Error is approximately 3%. [b] 80E is 80 vol % ethanol–20 vol % water, 70T is 70% 2,2,2-trifluoroethanol–30% water, and 90H is 90% 1,1,1,3,3,3-hexafluoro-2-propanol–10% water, etc. Solutions were 0.10 M in the starting compound and buffered with 2,6-lutidine.

of a solvolytic secondary-to-tertiary Wagner–Meerwein rearrangement which occurs after reversible intimate ion pair formation.

In the solvolysis of cyclopentyl *p*-bromobenzenesulfonate, secondary deuterium isotope effects in alcohol–water solvents indicate that the initially formed intimate ion pair can undergo recombination, substitution, elimination, or solvent separation.[4,5] The relative rates of these different reaction paths are dependent upon the ionizing strength and nucleophilicity of the alcohol–water solvent. In trifluoroacetic acid, Bunnett and Paradisi confirmed the importance of internal return in the cyclopentyl system by observing oxygen scrambling in the starting ester concurrent with solvolysis. In contrast the pinacolyl ester showed no such scrambling during solvolysis.[7]

Thus, it struck us as significant that 2,2-dimethylcyclopentyl *p*-toluenesulfonate (I-OTs) was reported to solvolyze in acetic acid more slowly (0.86 times as fast) than cyclopentyl *p*-toluenesulfonate (II-OTs) even though the products of the former were largely rearranged.[8] Since 2-methyl substitution should inductively accelerate ionization, these observations suggest the possibility that every ionization in I-OTs is *not* followed by rearrangement and that solvolysis is slowed by ion pair return. The relatively slow rate of methyl migration in this system was demonstrated by Wilcox in the acid-catalyzed rearrangement of cyclobutyldimethylcarbinol to 2,2-dimethylcyclopentanol[9] and suggested to us that the 2,2-dimethylcyclopentyl cation was formed as an intermediate and combined with water faster than it rearranged. This reluctance to rearrange could be attributed to the strain required for the β carbon–carbon bond to become aligned parallel with the vacant p orbital of the α carbon.[10] We have examined this problem more closely through a detailed study of the rates and products of solvolysis of 2,2-dimethylcyclopentyl *p*-bromobenzenesulfonate (I-OBs) and have determined the effects of α- and β-deuterium substitution on the solvolysis rates.

Table II. First-Order Rate Constants[a] and Deuterium Isotope Effects in Solvolysis of 2,2-Dimethylcyclopentyl *p*-Bromobenzenesulfonate (I-OBs) at 25 °C

solvent[b]	k_H	$k_H/k_{\alpha\text{-}d}$	$k_H/k_{\beta\text{-}d_2}$	k_1/k_{cp}[c]	k_1/k_{pin}[c]
80E	2.722	1.186	1.260	0.194	4.28
70E	7.065	1.204	1.251	0.254	4.07
70T	51.73	1.201	1.256	1.60	4.86
97T	42.35	1.198	1.270	4.04	5.31
90H	274.9	1.201	1.300	10.0	5.58

[a] k's are in units of 10^{-5} s^{-1}, measured spectrophotometrically at 25 °C. All kinetic runs are in duplicate except for 80E. Error on isotope effects is less than 0.005. [b] Solvents are as described in Table I. [c] The last two columns are rate ratios relative to the corresponding cyclopentyl and pinacolyl esters, respectively.

Results and Discussion

Product studies in solvents ranging in nucleophilicity from 80% ethanol–water (80E) to 90% 1,1,1,3,3,3-hexafluoro-2-propanol (90H) are summarized in Table I. Typically, 2,2-dimethyl-1-deuteriocyclopentyl *p*-bromobenzenesulfonate was solvolyzed at 25 °C in sealed NMR tubes in the presence of buffer for more than 10 half-lives. The product mixtures were analyzed directly from their NMR spectra by assignment of the deuterium chemical shifts of the known products. The results from Table I are especially significant on two points. First, the very high percentage of rearranged products (IV, V, and VI) was largely independent of solvent nucleophilicity, and second, there was no detectable evidence for unrearranged substitution product in any of these solvents.

Table II summarizes the α-*d* and β-d_2 kinetic isotope effects in the solvolysis of I-OBs. The α-*d* effects in all solvents are around 1.20, higher than the 1.15–1.16 value for pinacolyl *p*-bromobenzenesulfonate, which is characteristic of rate-determining ionization.[3a] The isotope effects are, however, lower than the maximum value of 1.23 expected for rate-determining solvent separation of the intimate ion pair.[4] Its size (1.20) is qualitatively consistent with expectations for rate-determining rearrangement after reversible formation of the intimate ion pair;[11] in this transition state the stiffness of the α-hydrogen bond is increased by the partial bond between the α carbon and the β methyl group.[12]

A similar picture emerges from a consideration of the β-d_2 effects, which are around 1.26. The small yield (3–6%) of unrearranged alkene, which would be formed from the ion pair with a primary isotope effect of about 2.0, causes the measured effect to be a few percent higher than if all the reaction involved rearrangement. Thus, the β-d_2 effect for rate-determining rearrangement is about 1.24. This value is slightly higher than the 1.20 β-d_3 value for the pinacolyl ester[3a] and about the same as the 1.24 value for rate-determining ionization in the cyclopentyl ester. It is, however, lower than the 1.48 value estimated for rate-determining separation of the intimate ion pair for cyclopentyl ester.[13] Since the β-d_2 effect is of hyperconjugative origin[14] and responds directly to the degree of orbital vacancy on the α carbon, we conclude that methyl participation is better at reducing this vacancy than it is at restoring the bending force constant at the α carbon. This would be expected if the transition state for participation involved π-bonded resonance contributing forms.[15,16]

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(5) Using relative rate correlations, it has been proposed that the cyclopentyl sulfonate ion pair intermediate is nucleophilically solvated and that internal return, although in principle allowed, is not kinetically significant.[6]

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(11) A simplex treatment of the stepwise isotope effects[4] shows the isotope effect for methyl migration in 1-deuterio-2,2-dimethylcyclopentyl cation to be 0.97.

(12) Shiner, V. J., Jr.; Fisher, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 2553–2554.

(13) The β-d_2 value for ionization is not directly observed but can be calculated from the isotope effects for the single steps of the mechanism given in Table II of ref 4. When the values of column 3 are used, the effect is calculated as $1.10 \times 1.128 = 1.24$; similarly the value for rate-determining separation of the intimate ion pair is $(1.10 \times 1.128)/(0.91 \times 0.92) = 1.48$. The figures from columns 1, 2, and 4 give similar results.

(14) Collins, C. J.; Bowman, N. S. "Isotope Effects in Chemical Reactions"; Van Nostrand Reinhold; New York, 1970; pp 137–148.

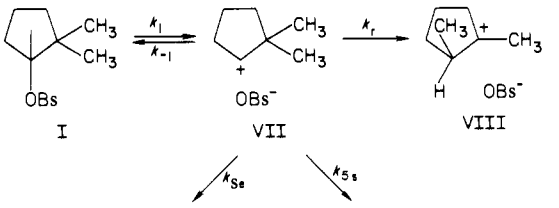
Thus, in summary, for these two cyclopentyl compounds, the overall isotope effects for rate-determining ionization, rate-determining methyl migration after ionization, and rate-detemining solvent separation are about 1.15, 1.20, and 1.23 for α deuteration and about 1.23, 1.24, and 1.48 for β dideuteration, respectively.

The near constancy of both the α-d and β-d_2 isotope effects and the percent rearranged products in solvents of differing ionizing power and nucleophilicity argue for a single, dominant mechanism for the solvolysis of 2,2-dimethylcyclopentyl brosylate (I-OBs). This contrasts dramatically with the solvolytic behavior of cyclopentyl brosylate (II-OBs) where isotope effects and product mixtures vary with with changes in solvent properties.[16]

The importance of internal return in the solvolysis of 2,2-dimethylcyclopentyl brosylate (I-OBs) can be confirmed independently of the above isotope effect data by recalling previously reported evidence for internal return in cyclopentyl p-bromobenzenesulfonate (II-OBs), which was the most compelling in 90H.[16] Under these conditions, the reaction of II-OBs is mainly that of syn elimination, and the α-d effect is at a maximum value of 1.23. The β-d effects are large and noncumulative, with the *cis* β-d effect being larger than the *trans*. These data taken together indicate that II-OBs reacts by rate-determining elimination from the intimate ion pair. In HFIP internal return is at a maximum and internal syn elimination occurs before formation of the solvent-separated ion pair. These conclusions are consistent with the observation of internal return in the oxygen scrambling experiments of Bunnett and Paradisi in the solvolysis of cyclopentyl benzenesulfonate in TFA.[7] Now, if one accepts, based upon the above evidence, that cyclopentyl brosylate is undergoing internal return in 90H, then by using relative rate data (I-OBs/II-OBs) one must conclude that 2,2-dimethylcyclopentyl brosylate is also undergoing internal return. In 90H the dimethyl compound, I-OBs, solvolyzes only 10 times faster than cyclopentyl, II-OBs (Table II). This factor of 10 is easily accounted for by the inductive effects of two β methyl groups.[17] Further acceleration of ionization due to the eclipsing strain of the β methyl groups may also be a contributing factor. Thus, since cyclopentyl brosylate is undergoing internal return in 90H, 2,2-dimethylcyclopentyl brosylate must also be, or it would solvolyze much more than 10 times faster.

Recently, much solvolytic work has been interpreted by a mechanism which suggests that ionization can be assisted by either solvent (k_s) or neighboring group (k_Δ) or can occur without assistance (k_c).[18-20] This scheme, however, is not adequate in explaining the results from both the product and kinetic studies of the solvolysis of 2,2-dimethylcyclopentyl p-bromobenzenesulfonate (I-OBs). The k_s classification does not account for our observation that the high percentage (>90%) of rearranged product is constant and unaffected by changes in solvent nucleophilicity. If the solvent was covalently bonding to the reactive carbon, one would expect less rearrangement in more nucleophilic solvents and perhaps some unrearranged substitution product. Neither is observed. The only unrearranged product, 3,3-dimethylcyclopentene, is from elimination. Similarly the α-deuterium isotope effect shows no variation with change in solvent nucleophilicity. If a k_s process was operative, one would observe smaller values for the isotope effect in more nucleophilic solvents.[3d] Also, the constant α-deuterium effect of 1.20 is too large for a transition state involving significant covalent bonding by nucleophile to the reactive carbon. When our kinetic data are examined using the "ethanol–trifluoroethanol" criteria of Harris and Raber,[21] one finds only a slight deviation between the water–ethanol plot and the water–trifluoroethanol plot.[22] The near fit is inconsistent with a k_s process and instead suggests that I-OBs reacts by a "limiting" process (k_c or k_Δ).

Scheme I



On the other hand, interpretation of the kinetic results as a simple k_c process suffers from the problem of why the α-deuterium isotope effect is different from the value for the pinacolyl (rate-determing formation of the tight ion pair) and 2-adamantyl esters (rate-determing formation of the solvent separated ion pair). Likewise, from the rate data relative to the cyclopentyl system and from arguments made earlier, it is clear that the 2,2-dimethyl system solvolyzes with significant amounts of internal return. A k_c interpretation does not allow for kinetically significant amounts of internal return. If we fit our data to the solvolytic blending parameter, Q', used by Schleyer and Bentley, we obtain a value of 0.72, which is too small to be interpreted as a k_c process.[6]

Finally, if we explain the reactivity of I-OBs by a k_Δ process, we cannot account for the very little rate acceleration relative to the cyclopentyl analogue in nonnucleophilic solvents and an α-deuterium isotope effect (1.20) which is larger than the expected value of less than 1.15. Earlier work by Wilcox also demonstrated the relatively slow rearrangement of the 2,2-dimethylcyclopentyl cation. Thus, we conclude that none of these three possibilities (k_s, k_c, or k_Δ) by themselves is sufficient to explain all our observations (products and kinetics) for the solvolysis of I-OBs.

We prefer to incorporate these rate constants as part of Winstein's ion pair scheme and find this presentation more suitable for explaining all the experimental data.[23,24] Thus, in Scheme I, 2,2-dimethylcyclopentyl brosylate (I-OBs) ionizes to form the intimate ion pair VII, which undergoes return, k_{-1}. Because it is sterically hindered from nucleophilic substitution, k_{5s}, VII undergoes rate-determining rearrangement, k_r. The constancy of the product ratios and isotope effects in a wide spectrum of solvents suggests that nucleophilic substitution on ion VII does not compete well wtih methyl migration, even in solvents as nucleophilic as 80E. On the other hand, because of the slightly unfavorable stereoelectronic arrangement in the 2,2-dimethylcyclopentyl cation, methyl migration is slower than ion pair return.

Relative rate comparisons with cyclopentyl brosylate further demonstrate the insensitivity of I-OBs to solvent nucleophilicity. In the more nucleophilic solvents, cyclopentyl, which is sterically unhindered, reacts faster, but in TFE and HFIP solvents, which

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(17) Schleyer has argued that the acclerating effects in such nonnucleophilic solvents should be much higher.[3c,d]

(18) As orginally proposed by Winstein,[19] k_s, k_Δ, and k_c are rate constants for single step processes involving, respectively, solvent assisted, anchimerically assisted, and unassisted ionization. For a different view of the role of solvent, Swain and co-workers concluded in a study of 77 reactions in 61 solvents that chemical reactivity can be correlated by relating the anion and cation solvating properties of the solvent to a set of reaction constants. These workers found that "solvent effects afford no operational distinction between nucleophilic assistance (covalent bonding) and cation solvation (ionic bonding) by the solvent".[20]

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(22) We have chosen to evaluate the correlation between the two plots by measuring the difference in log k units of the 97 TFE point from its "expected" position on the water–ethanol plot. Differences, Δ97T, of less than 0.5 correspond to systems which Raber and Harris have identified as "limiting", no external nucleophilic assistance. It should be pointed out that the fit of the TFE points on the ethanol plot can be strongly affected when the leaving group of the system studied differs from the reference compound, usually 1-adamantyl bromide. For example, plotting 2-adamantyl brosylate against 2-adamantyl tosylate gave Δ97T = 0.40. On the other hand, 1-adamantylmethylcarbinyl brosylate against the corresponding tosylate gave Δ97T = 0.10.

(23) In the ion pair scheme, k_s corresponds to k_4, k_c to k_1, and k_Δ to an implied $k_{4\Delta}$.

(24) Tipson, R. S. *J. Org. Chem.* **1944**, *9*, 235–241.

are nonnucleophilic, the dimethyl compound I-OBs is faster. This observation is nicely in accord with the conclusion that in the dimethyl compound, internal return is faster than rearrangement.

The near constancy of the rate ratios of I-OBs to pinacolyl brosylate is also consistent with our mechanism. In both systems solvent is not involved nucleophilically before or during the rate-determining step (k_4 or k_{5s}), and therefore, the relative rates should not change with variation in solvent nucleophilicity. The rates are affected primarily by changes in the ionizing strength of the solvent and to nearly the same extent because of the similarities in charge separation in the two rate-determining transition states. For pinacolyl sulfonates, the rate-determining step is simple ionization to the tight ion pair and the transition state resembles the ion pair. In the case of 2,2-dimethylcyclopentyl brosylate, the rate-determining step is the exothermic rearrangement of the secondary to the tertiary cation, and according to the Hammond postulate, this transition state should also resemble the ion pair.

Experimental Section

Spectra. ^2H NMR spectra were recorded by using a Varian 220 spectrophotometer operating at 33.8 MHz. Chemical shifts were determined relative to tetramethylsilane-d_{12}. All solutions were approximately 0.1 M in the deuterated compound studied, and solutions were buffered with an equivalent of 2,6-lutidine. Chemical shifts were as follows: 3,3-dimethyl-2-deuteriocyclopentene (5.85 ppm), 2,3-dimethyl-3-deuteriocyclopentene (2.74 ppm), and 2,3-dimethyl-2-deuteriocyclopentanol (1.95 ppm). 1,2-Dimethylcyclopentene was determined from the amount of O-deuterated solvent (5.35 ppm).

2,2-Dimethylcyclopentyl *p*-Bromobenzenesulfonate (I). 2,2-Dimethylcyclopentanol was prepared by using the procedure of Wilcox and Mesirov.[9] The corresponding brosylate was prepared by using the Tipson procedure,[24] mp 48-50 °C.

Deuterated 2,2-Dimethylcyclopentanols. 1-Deuterio-2,2-dimethylcyclopentanol was prepared by treating 1.8 g of 2,2-dimethylcyclopentanone with 0.7 g of lithium aluminum deuteride. 5,5-Dideuterio-2,2-dimethylcyclopentanol was prepared by lithium aluminum hydride reduction of the corresponding ketone. 5,5-Dideuterio-2,2-dimethylcyclopentanone was prepared from the exchange reaction of 2,2-dimethylcyclopentanone and D_2O in the presence of anhydrous K_2CO_3. The exchange reaction was repeated 5 times.

Kinetic Measurements. Rate measurements were made by using a Cary 118A spectrophotometer. The reactions were carried out in stoppered 1-cm^2 quartz cells in a specially constructed, thermostated, brass block holder. The procedure and technique have been described previously.[16]

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Registry No. D_2, 7782-39-0; 2,2-dimethylcyclopentyl *p*-bromobenzenesulfonate, 94844-04-9; 2,2-dimethylcyclopentanol, 37617-33-7; 1-deuterio-2,2-dimethylcyclopentanol, 94844-05-0; 2,2-dimethylcyclopentanone, 4541-32-6; 5,5-dideuterio-2,2-dimethylcyclopentanol, 94844-06-1; 5,5-dideuterio-2,2-dimethylcyclopentanone, 94844-07-2.

Intramolecular Carbopalladation of Allylic Amines and Sulfides

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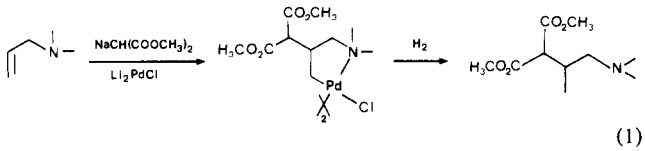
Abstract: β-Malonyl allyl sulfides and amines have been found to cyclize in the presence of lithium tetrachloropalladate and base to regiospecifically and stereospecifically provide fused bicyclic palladocycles which are converted to cyclopentanes upon hydrogenation. The cyclization may be extended to generate six- and seven-membered rings in high yield. Cyclization to provide cyclic ketones also occurs in high yield.

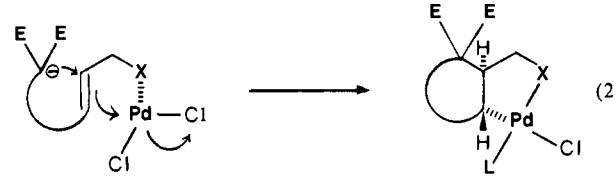
We have previously reported that allylic[1] and homoallylic[2] amines and sulfides undergo regiospecific carbopalladation in the presence of stabilized enolates and lithium tetrachloropalladate (LTP) to provide stable five-membered palladocyles (eq 1). The



(1)

palladium atom in these palladocycles may subsequently be replaced by carboxylate[3] (CO, CH_3OH), by hydrogen[1] (H_2, $NaBH_4$, or $NaBH_3CN$), or by a substituted vinyl group[4] (MVK, Et_3N). We have demonstrated that the carbopalladation process occurs in a stereospecific manner, introducing malonate and palladium in a trans fashion across the unsaturated linkage.[5,6]

We expected the intramolecular version of the carbopalladation reaction to provide a new method for the regiospecific construction of carbocyclic structures with concomitant stereochemical control at at least two contiguous carbon centers.[7] For example, allylic amines or sulfides should cyclize to provide bicyclic intermediates in which the ring juncture stereochemistry is governed by the stereochemistry of the allylic double bond (eq 2). We report



(2)

herein the successful realization of this objective, providing new methodology for the generation of carbocyclic compounds from acyclic allylic sulfides and amines.

The initial phase of this study required a variety of substrates encompassing both cis and trans allylic amines and sulfides potentially capable of cyclizing to provide carbocycles of several different sizes. For this purpose cis substrates **4a-g** and trans substrates **9a-f** (Scheme I) were prepared by using standard methodology. Preparation of these substrates was generally straightforward and, with one exception, requires no further comment.

We were fortunate to find that *cis*-olefins **7a** and **7b** (readily available by hydrogenation of **1a** and **1b**) served as convenient precursors of trans substrates **9a-f**. Conversion of **7a** or **7b** to the mesylate or dimesylate followed by treatment with excess sodium iodide led to formation of a ca. 3:1 equilibrium mixture

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