4 H), 3.8 (s, 2 H), 2.9 (s, 6 H); MS (70 eV), *m/e* 211 (M^+), 193, 167 ($M^+ - N(CH_3)_2$), 166, 165, 152, 134 [$CH_2C_6H_4N(CH_3)_2$], 91 ($C_6H_5CH_2$).

Competition Studies. Relative Rate Constants. The relative rate constants for the reaction of $O_2^{-}\cdot$ with diphenylmethanes **2** were determined by a series of competition reactions. Potassium superoxide (1.5 mmol) wad added to a benzene solution (30 mL, Na-dried) containing 0.125 mmol of each competitor, crown ether (1.25 mmol), and the internal standard diphenylacetylene (0.125 mmol). The reaction vessel was capped with a septum, and the reaction mixture was magnetically stirred at ambient temperature. For each pair of reactants, four or five samples were removed at appropriate intervals during the course of the reaction and quenched with 10% HCl. The organic phase of each sample was then analyzed by GLC at least thrice with the relative rate constants for the disappearance of the competitors calculated from their respective GLC peak areas using equation 8. Table II shows the VPC conditions and the results of these competitions.

Isotope Effects. The isotope effects for diphenylmethanes **2a** and **2g** were determined by ^{1}H NMR analysis of competition reactions between the protio ($ArCH_2$) and deuterio ($ArCD_2$) analogues, as follows. A mixture of **2** (**a** or **g**), its deuterio analogues and hexamethylbenzene in an appropriate molar ratio of 5:5:1 was prepared and analyzed by ^{1}H NMR. The relative integrations of the benzyl methyls of the standard, the diarylmethylene hydrogens of the protio compounds, and the aromatic hydrogens due to both the protio and deuterio species permitted a determination of the ratio of standard:protio analogue:deuterio analogue prior to reaction ($t = 0$). An aliquot of this mixture, containing 1.25 mmol of each competitor, 0.25 mmol of standard, and 12.5 mmol of 18-crown-6 polyether was dissolved in 300 mL of sodium-dried benzene to which 15 mmol of KO_2 were subsequently added. After 2–3 h, the reaction mixture was quenched with 10% HCl, neutralized with $NaHCO_3$, washed 4 times with water (to remove all traces of crown ether), and dried over $MgSO_4$. The solvent was evaporated and the residue, containing unreacted starting materials, internal standard, and products, was dissolved in CCl_4 and analyzed again by ^{1}H NMR. The relative integrations of the benzylic methyl absorption of the standard versus the diarylmethylene absorption of the protio species indicated the extent of reaction of the latter. The unreacted starting material was collected by preparative GLC (3 ft × $^1/_4$ in. copper column packed with 10% FFAP on chromosorb PAW DMCS) and analyzed by ^{1}H NMR. The relative integrations of the methylene and aromatic absorptions indicated the relative amounts of unreacted protio and deuterio analogues. Combining the information from the two NMR analyses following workup permitted the determination of the ratio of standard:protio analogue;deuterio analogue following reaction. The isotope effect (k_H/k_D) was then calculated using the equation

$$k_H/k_D = \frac{\log (H_i/H_f)}{\log (D_i/D_f)}$$

where H_i, H_f, D_i, D_f are the relative initial and final amounts of protio and deuterio compounds.

Concentration Effects. Three 50-mL round-bottomed flasks were each charged with 20 mL of sodium-dried toluene and 110 mg (1.5 mmol) of KO_2 but differing amounts of 18-crown-6, namely 330 mg (1.25 mmol), 247 mg (0.938 mmol), and 165 mg (0.675 mmol), respectively. The reaction vessels were capped with rubber septa and magnetically stirred for 1 h to assure saturation. In addition, a stock solution was prepared containing equimolar amounts of 4-chlorodiphenylmethane (**2e**) and diphenylacetylene (as internal GLC standard). Reaction commenced simultaneously in each flask upon addition of an aliquot of this stock solution containing 0.125 mmol of **2e** and 0.125 mmol of diphenylacetylene. For each concentration, samples were removed from the reaction vessels at time $t = 0$, 24, 48 and 72 h, and the reaction in each sample was quenched with 10% HCl. The organic phase of each sample was then analyzed at least thrice by GLC (3 ft × $^1/_2$ in. glass column packed with 15% FFAP on chromosorb PAW DMCS at 200 °C) to determine the relative rate of disappearance of starting material. These were then compared to the results obtained for similar reaction times at other concentrations. These series of simultaneous reactions were repeated 4 times, and the results obtained had a precision of ±10%.

Note Added in Proof: In the closing paragraph of the Introduction we noted the low *D*(R–H) value of 66 kcal/mol reported by Benson and O'Neil[14] of diphenylmethane. Professor Benson has recently communicated to us that this value was based on pyrolysis data for diphenylacetic acid which was undoubtedly in error by about 10 kcal. He agrees, therefore, with the current[17,18] value of 81 kcal/mol. This revised *D*(R–H) value will affect the predicted electron affinity of the diphenylmethyl radical reported by McMahon and Kebarle.[13]

Acknowledgment. We would like to express our heartfelt gratitude to Professor Shmaryahu Hoz for sharing with us his creative and insightful thoughts on the issues raised in this paper.

Registry No. **1i**, 2243-80-3; **1j**, 1503-49-7; **2a**, 101-81-5; **2b**, 834-14-0; **2c**, 620-83-7; **2d**, 457-68-1; **2e**, 831-81-2; **2f**, 2116-36-1; **2g**, 101-76-8; **2g**-deutero, 101419-03-8; **2h**-deutero, 56652-42-7; **2i**, 5840-41-5; **2j**, 23450-31-9; **2k**, 1817-77-2; D_2, 7782-39-0; superoxide, 11062-77-4.

The Nickel Promoted 1,3-Migration of an sp^2 Center: Ring Expansion of a Vinylcyclobutene

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The nickel tetracarbonyl promoted rearrangement of dimethyl 3-vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate (1) to dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate (2) proceeds in two distinct steps involving dimethyl 3-vinylcyclobutene-1,2-dicarboxylate (5) as an isolable intermediate. Both steps require the presence of the transition metal. Deuterium labeling shows that it is an sp^2 center and not an sp^3 center of the vinylcyclobutene which undergoes the migration.

Introduction

Due to our interest in transition metal promoted rearrangements, we became intrigued by a report in which dimethyl 3-vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate (1) undergoes a ring expansion, with concomitant loss of the chlorines, to give dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate, (2) upon treatment with nickel tetracarbonyl in refluxing benzene/dimethylformamide.[1] The net result of this ring expansion reaction, regardless of its mechanism, is a nickel promoted 1,3-sigmatropic shift. Although there

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[1] Scharf, H.-D.; Korte, F. *Chem. Ber.* **1966**, *99*, 1299, 3925.

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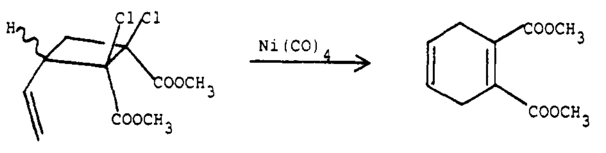

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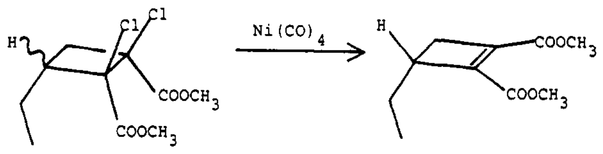


3 4

are numerous examples in the literature[2] of transition metal catalyzed or promoted 3,3-sigmatrophic shifts (Cope rearrangements), this is one of only a few reactions which has as its net result a metal promoted or catalyzed 1,3-alkyl shift.[3-9] In addition, this result is in contrast to the 3-ethyl analogue which simply loses the chlorines.

In this paper, it will be shown that the dechlorination and the ring expansion occur in separate steps in the conversion of 1 to 2, and that both the dechlorination step and the ring expansion step require nickel tetracarbonyl.

Results

The synthesis of dimethyl 3-vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate (1) was accomplished by the literature method.[1] The first step is a triplet-sensitized (2 + 2) photochemical cycloaddition between dichloromaleic anhydride and butadiene. The product anhydride is hydrolyzed to the diacid and then esterified with diazomethane to give the diester (Scheme I). Due to the nature of the synthesis, the chlorines must be cis, but can be either cis or trans to the vinyl group. The isomeric ratio for different runs fluctuates between 50:50 and 60:40 (the stereochemistry of the major isomer is unknown). This mixture of isomers is used for all further reactions.

When vinylcyclobutane 1 is allowed to react with nickel tetracarbonyl in benzene and dimethylformamide at reflux for 4 h as originally reported,[1] a 52% yield of dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate (2) is obtained.

To ensure the authenticity of the product, in particular the 1,4 relationship of the diene, an independent synthesis using a Diels–Alder reaction was desired. It was found that the Diels–Alder reaction can be accomplished in either of two ways (Scheme II). In the first, butadiene sulfone and dimethyl acetylenedicarboxylate were allowed to reflux in xylene for $2^1/_2$ h. In the second synthesis, butadiene and dimethyl acetylenedicarboxylate were mixed in dioxane in a sealed tube, and allowed to stand at room temperature for 5 days. In both procedures, the product was distilled from the reaction mixture.

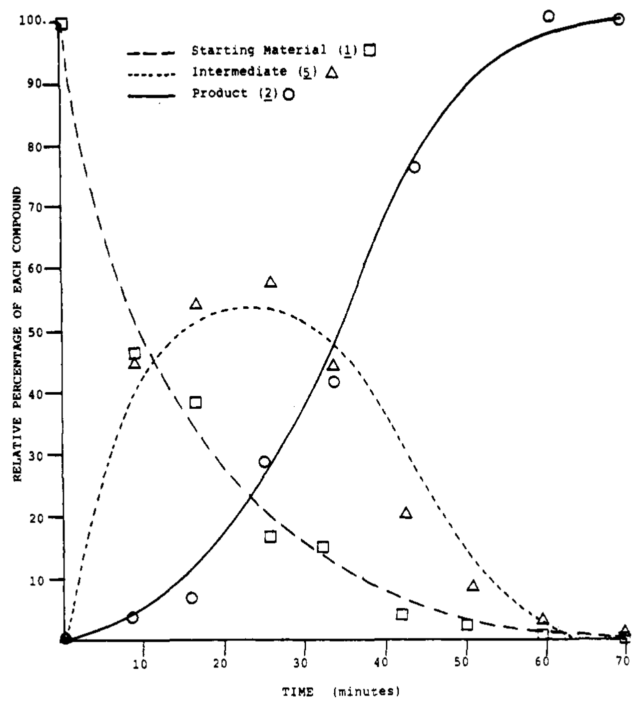
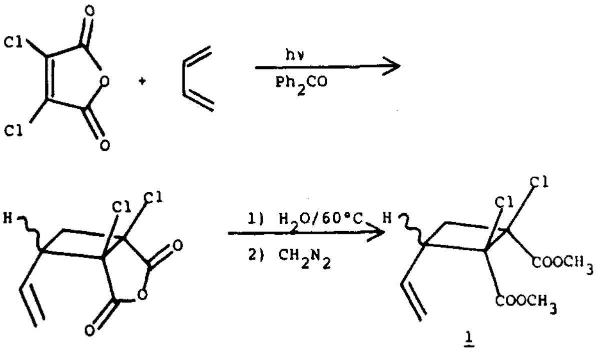


Figure 1. Relative percentage of each compound vs. time for the reaction of dimethyl 3-vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate with nickel tetracarbonyl.

Scheme I



The product from each of the Diels–Alder reactions and the product from the organometallic reaction have the same NMR spectra. In addition, these spectra are in agreement with a literature spectrum of the ethyl ester analogue.[10] Thus, the product definitely contains a nonconjugated diene.

Control experiments were run to determine if both nickel tetracarbonyl and dimethylformamide are indeed needed to effect the ring expansion reaction. If dimethylformamide is omitted and additional benzene is added to maintain a constant volume, only a trace of the product is observed. Likewise, if nickel tetracarbonyl is omitted and additional benzene is added, there is no observable product formation.

To confirm which bond of the four-membered ring migrates, a deuterated analogue was synthesized. Butadiene sulfone-d_4 was pyrolyzed to give butadiene-d_4, which in turn, was photolyzed in the presence of dichloromaleic anhydride and benzophenone as described above. The

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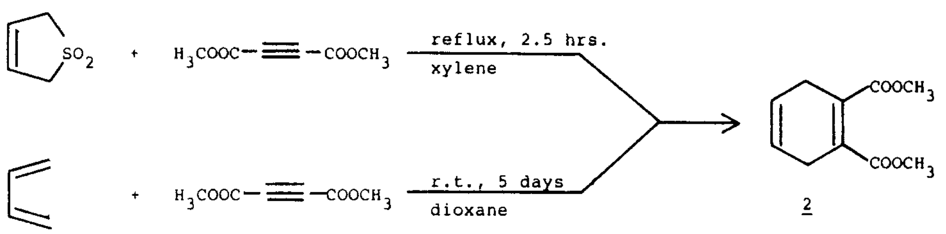
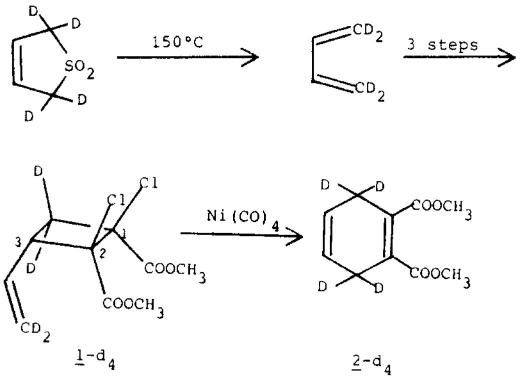
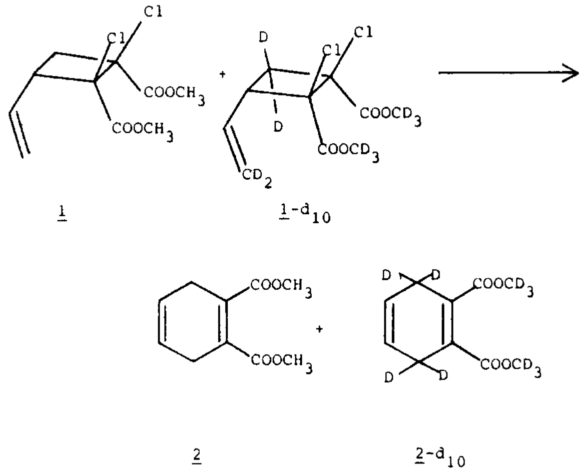
Scheme II



Scheme III



Scheme IV



product from this reaction was then hydrolyzed and esterified to give the tetradeuterated analogue of the starting vinylcyclobutane (Scheme III). Upon reaction with nickel tetracarbonyl, this deuterated compound gives dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate-d_4 with the deuterium at the 3 and 6 positions only. This result is only possible if it is the 2,3-bond of the starting material which migrates.

To learn if there is an intermediate in the conversion of the starting material to the product, the reaction was monitored using gas chromatography by removing aliquots from the reaction mixture at various times. The graph shown in Figure 1 is a plot of the relative percentage of each material vs. time. As can be seen, there is an exponential decay of the concentration of the starting material. The concentration of an intermediate is found to increase for about 25 min and then to steadily decline. The product begins to appear only after about 15 min, and then its concentration sharply increases. The onset of this increase in the product concentration coincides with the concentration of the intermediate being near its maximum.

Running the ring expansion reaction in refluxing tetrahydrofuran/dimethylformamide with a very large excess of nickel tetracarbonyl allows the intermediate to be isolated, but unfortunately, always contaminated by some product. From various runs, the intermediate to product ratio varies from 60:40 to 95:5. In order to isolate the reaction intermediate, the nickel tetracarbonyl must be removed *before* the reaction mixture is subjected to a water workup. Removal of the nickel tetracarbonyl is accompanied by distilling it from the reaction mixture at atmospheric pressure. Once this is done, the reaction mixture can be worked up in the usual manner. On the basis of its spectral data, the reaction intermediate is dimethyl 3-vinylcyclobutene-1,2-dicarboxylate (5).

To confirm that this vinylcyclobutene can be converted to the reaction product, a 72/28 mixture of that compound and the product cyclohexadiene was heated with nickel tetracarbonyl under the standard conditions. Within 26 min, the intermediate was shown by gas chromotography to have been quantitatively converted to the product.

Similarly, a 62/38 mixture of the vinylcyclobutene and the cyclohexadiene was heated under standard conditions but in the absence of nickel tetracarbonyl. Monitoring this reaction by gas chromatography revealed that after $3^1/_2$ the amount of product remains the same, while during this same time period, the intermediate virtually disappears due to decomposition to polymeric material.

A 76/24 mixture of the vinylcyclobutene and the cyclohexadiene was heated under the standard condition but in the absence of dimethylformamide. The results of this reaction are the exact same as those obtained from the reaction of the vinylcyclobutene and nickel tetracarbonyl run in the presence of dimethylformamide.

Finally, to determine if free butadiene and dimethyl acetylenedicarboxylate, generated by a metal-induced retro-(2 + 2) reaction of 5 are involved in this rearrangement, a double labeling experiment was performed. Starting with vinylcyclobutane-d_0 and vinylcyclobutane-d_{10}, only cyclohexadiene-d_0 and -d_{10} are observed (Scheme IV). Thus, any mechanism proposed must involve an organometallic intermediate which does *not* undergo ligand exchange.

Discussion

Unlike the one-step mechanism previously proposed,[1] it has been found that the conversion of vinylcyclobutane 1 to cyclohexadiene 2 proceeds in two distinct steps. The first is a dechlorination to give a vinylcyclobutene (5) and the second is a ring expansion to give the product cyclohexadiene. Both steps require the presence of nickel tetracarbonyl.

The first step is the same reaction as that observed for the 3-ethyl analogue.[1] The exact nature of this dechlorination is unknown, but the requirement of dimethylformamide for only this step suggests a single electron transfer process.[11]

The more intriguing step is the second one. Based upon deuterium labelling studies, it is the 2,3-bond of the dichlorovinylcyclobutane which migrates, so therefore, it is also the 2,3-bond of the vinylcyclobutene which migrates.

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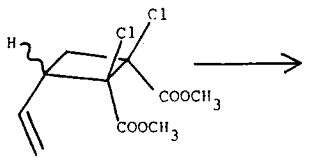

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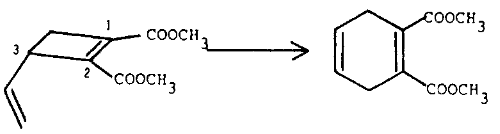

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2

Thus, this reaction is one of the rare cases of a non-phenyl-sp^2 center undergoing a net 1,3-sigmatropic shift.[2,12]

Some other examples of this net rearrangement include work on the thermal[13] and acid catalyzed[14] 1,3-acyl shift. Most relevant to this study is the work on the photochemical[15,16] and thermal[17] conversion of substituted vinylcyclopropenes to the corresponding cyclopentadiene. The temperatures required for these thermal reactions are 340 °C for the acyl migration and 180 °C for the vinylcyclopropene rearrangement. In addition, the ring opening of dimethyl cyclobutene-1,2-dicarboxylate to the corresponding butadiene derivative requires 165 °C.[18] Since these temperatures are 85 to 260 °C higher than the temperatures used for the nickel-assisted vinylcyclobutene rearrangement, it is not surprising that no rearrangement of any type was observed in the absence of nickel tetracarbonyl.

Although this reaction involves a net 1,3-shift, the detailed mechanism of the nickel-promoted vinylcylobutene rearrangement is presently unknown. However, experiments are now in progress to gain more information about the mechanism of this rearrangement. In addition, a more easily manageable nickel(0) source, to replace nickel tetracarbonyl, is being sought.

Conclusion

Dimethyl 3-vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate upon treatment with nickel tetracarbonyl in benzene and dimethylformamide eliminates the chlorines to give dimethyl 3-vinylcyclobutene-1,2-dicarboxylate, which then undergoes a nickel promoted ring expansion to generate dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate.

Experimental Section

Dioxane, benzene, and tetrahydrofuran were freshly distilled from benzophenone ketyl. Dimethylformamide was distilled from barium oxide and stored under argon. All reactions were carried out using oven dried glassware that was cooled under an argon atmosphere. All reactions were run under an argon atmosphere.

Gas chomotographic analyses were performed using a Hewlett-Packard Model 5890A spectrometer with a 6 ft × $^1/_8$ in., 3% OV-17 column, flame ionization detector, and temperature programming (initial oven temperature = 70 °C, increased at 10 °C/min to 100 °C, and then increased at 2 °C/min to 145 °C), retention times: 12.6 min for the vinylcyclobutene, 17.6 min for the cyclohexadiene, and 18.0 and 18.2 min for the starting material isomeric mixture.

Nuclear Magnetic Resonance spectra were recorded on a Nicolet 300-MHz NMR spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 599 IR spectrophotometer. Mass spectra were recorded on either a Hewlett-Packard Model 5995 or a Kratos model mass spectrometer.

Dimethyl 3-Vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate. To a 100-mL-capacity thick-walled phototube was added dihloromaleic anhydride (1.84 g, 11.0 mmol), benzophenone (0.132 g, 0.7 mmol), and dioxane (19.2 mL). The resulting solution was frozen in a −78 °C bath and butadiene (4.8 mL, 55.0 mmol) was condensed into the phototube. The tube was then sealed and allowed to warm to room temperature. The reaction mixture was photolyzed for 72 h in a Rayonet photoreactor using 350-nm bulbs. At the end of this time, the tube was opened and the solvent was removed by vacuum distillation. The resulting crude anhydride mixture was hydrolyzed with distilled water (20 mL) at 60 °C for 10 m. The mixture was then made basic at ice-bath temperatures with a 2 N sodium hydroxide solution and washed with three 10-mL portions of ether. The aqueous layer was then acidified with 10% sulfuric acid and extracted with three 10-mL portions of ether. The ether extracts were combined and dried with magnesium sulfate. After the ether was removed, a yellow oil was obtained (1.64 g, 6.9 mmol, 62% yield of the diacid).

All of the above diacid was dissolved in 5 mL of ether and the resulting solution was stirred at ice-bath temperature. A cold diazomethane/ether solution was added dropwise until bubbling ceased and the solution remained yellow. This solution was then allowed to warm to room temperature and to stir overnight. Excess diazomethane was removed by water aspirator vacuum. Additional ether was added to this ether solution of the diester to obtain a total volume of 20 mL. The diester solution was then filtered and dried with potassium carbonate. After removal of the solvent a yellow oil remained (1.42 g, 5.3 mmoles, 77% yield): ^{1}H NMR mixture of 2 isomers (δ, $CDCl_3$) 2.54 (m, 4 H), 2.93 (dd, 1 H), 3.08 (dd, 1 H), 3.77 (s, 3 H), 3.78 (s, 3 H), 3.79 (s, 3 H), 3.82 (s, 3 H), 5.21 (m, 4 H), 5.75 (sept, 1 H), 5.93 (sept, 1 H); ^{13}C NMR (δ, $CDCl_3$) 35.8, 37.6, 42.3, 47.5, 52.9, 53.3, 53.4, 53.8, 74.6, 75.3, 76.7, 77.6, 118.9, 119.4, 131.8, 134.1, 167.4, 168.3, 168.4, 168.9; IR (cm^{-1}, $CHCl_3$) 2960, 1750, 1430, 1275; MS (CI) 269 (9%), 267 (13%), 237 (9%), 235 (14%), 208 (9%), 198 (12%), 197 (97%) 174 (8%), 167 (12%), 166 (12%), 165 (100%), 151 (13%), 137 (19%), 123 (17%), 111 (22%), 97 (52%).

Ring Expansion of Dimethyl 3-Vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate. Into a three-necked flask were added 0.69 g (2.6 mmol) of the vinylcyclobutane diester, 3.69 mL (54.0 mmol) of benzene, 1.16 mL (15.0 mmol) of dimethylformamide, and 1.93 mL (15.0 mmol) of nickel tetracarbonyl. The mixture was allowed to reflux under an argon atmosphere for 4 h. The mixture was then allowed to cool to room temperature and 25–50 mL of ether was added. The solution was filtered and then washed repeatedly with water until washing resulted in a clear aqueous layer. The solution was dried with potassium carbonate, and the solvent was removed to yield an oil (0.27 g, 1.4 mmol, 52% yield): ^{1}H NMR (δ, $CDCl_3$) 2.98 (s, 4 H), 3.76 (s, 6 H), 5.70 (s, 2 H); ^{13}C NMR (δ, $CDCl_3$) 27.5, 52.2, 122.3, 132.6, 168.5; MS (CI) 197 (71%), 165 (100%), 137 (7%), 97 (12%), 85 (32%), 76 (25%), 71 (47%).

Synthesis of Dimethyl 1,4-Cyclohexadiene-1,2-dicarboxylate. Butadiene sulfone (1.93 g, 40 mmol) was dissolved in 8 mL of xylene. Dimethyl acetylenedicarboxylate (4.32 mL, 35 mmol) was added and the mixture was allowed to reflux under argon for 2.5 h. The product was distilled (88 °C/0.1 mmHg) from the reaction mixture: ^{1}H NMR (δ, $CDCl_3$) 2.99 (s, 4 H); 3.77 (s, 6 H); 5.70 (s, 2 H).

Second Synthesis of Dimethyl 1,4-Cyclohexadiene-1,2-dicarboxylate. Into a thick-walled tube cooled to −78 °C was added dimethyl acetylenedicarboxylate (2.2 g, 15.5 mmol), dioxane (6.5 mL), and butadiene (6.5 mL, 74.6 mmol). The tube was then sealed and allowed to stand at room temperature for 5 days. The tube was opened and excess butadiene was removed with a water aspirator vacuum. The remaining yellow solution was distilled

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(87 °C/0.1 mmHg): ^{1}H NMR (δ, $CDCl_3$) 2.99 (s, 4 H); 3.77 (s, 6 H); 5.70 (s, 2 H).

Dimethyl 3-Vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate-d_4. A mixture of butadiene sulfone (9.94 g, 84.1 mmol), potassium carbonate (0.11 g, 0.8 mmol), D_2O (10 mL, 0.6 mmol, 99.8% D), and dioxane (10 mL) was stirred at room temperature under argon for 48 h. At the end of this period, water and dioxane were removed by vacuum distillation. Fresh dioxane and D_2O were added and the mixture was again stirred under argon for 48 h. The process of removing the water and dioxane and replacing them with fresh D_2O and dioxane was repeated an additional 6 times. After the final removal of water and dioxane, the resulting white solid was pyrolyzed at 150 °C for 1.5 h. The resulting 4.7 mL (54.0 mmol) of 1,1,4,4-butadiene-d_4 was passed through a 20% sodium hydroxide solution to remove SO_2 and through a drying tube, and then condensed into a phototube containing the dichloromaleic anhydride (1.14 g, 5.7 mmol) benzophenone (0.08 g, 0.4 mmol), and dioxane (12 mL) at −78 °C. The resulting mixture was photolyzed, hydrolyzed, and esterified as described above to yield the deuterate vinylcyclobutane diester (0.1 g, 0.6 mmol, 10% yield): ^{1}H NMR integrations (δ, $CDCl_3$) 2.39–3.11 (0.22 H), 3.47–3.69 (1.02 H), 3.69–4.00 (6.00 H), 5.00–5.31 (0.04 H), 5.61–6.04 (0.80 H).

Ring Expansion of Dimethyl 3-Vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate-d_4. The cyclobutane-d_4 diester (0.16 g, 0.6 mmol), nickel tetracarbonyl (0.97 mL, 7.5 mmol), dimethylformamide (0.68 mL, 8.8 mmol), and benzene (1.78 mL, 20 mmol) were allowed to react as described above for the undeuterated material to yield 0.08 g (0.4 mmol, 67% yield) of dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate-d_4: ^{1}H NMR integrations (δ, $CDCl_3$) 2.89–3.10 (0.27 H), 3.51–3.99 (6.00 H), 5.60–5.94 (1.86 H). Calculated integrations if 100% 2,3-bond migration: 2.89–3.10 (0.26 H), 3.51–3.99 (6.00 H), 5.60–5.94 (1.82 H).

Monitoring the Ring Expansion Reaction. Vinylcyclobutane diester (0.2861 g, 1.00 mmol), benzene (1.4 mL, 16 mmol), dimethylformamide (0.46 mL, 6 mmol), nickel tetracarbonyl (0.77 mL, 6 mmol), and dodecane (internal standard, 0.0858 g, 0.5 mmol) were mixed in a three-necked flask and allowed to reflux as described above. The reaction was monitored by gas chromotography at various times (see Results section). After all the starting material had been converted to the product, about 70 min, the reaction mixture was worked up in the usual manner. The product mixtures from four separate reactions were combined and purified by freezing at 0 °C which fractionated the mixture into two layers: a yellow bottom layer and a white top layer which is the cyclohexadiene diester product. The product was then separated from the lower yellow layer to yield 0.1745 g (0.9 mmol, 22% yield) of the cyclohexadiene diester.

Isolation of Dimethyl 3-Vinylcyclobutene-1,2-dicarboxylate (5). Vinylcyclobutane diester (0.80 g, 3.0 mmol), tetrahydrofuran (2.0 mL, 24.6 mmol), dimethylformamide (7.0 mL, 90.4 mmol), and nickel tetracarbonyl (15.0 mL, 115.9 mmol) were mixed in a three-necked flask and heated to reflux under argon. When the ratio of the vinylcyclobutene to the starting material approached 60:40 as determined by gas chromotography, the nickel tetracarbonyl was removed by distillation at atmospheric pressure. After removal of the nickel carbonyl, there is no starting material remaining and the vinyl cyclobutene to cyclohexadiene ratio, as determined by gas chromotography, ranges from 60:40 to 95:5. The reaction mixture was then cooled to room temperature and worked up in the usual manner to give an average of 40% recovery (0.24 g) of the yellow oil vinyl cyclobutene/cyclohexadiene mixtures (spectral data are for the 95:5 mixture): ^{1}H NMR (δ, $CDCl_3$) 2.45 (dd, 1 H, J = 1.8, 15 Hz), 2.94 (dd, 1 H, J = 4.5, 15 Hz), 3.57 (m, 1 H), 3.80 (s, 3 H), 3.81 (s, 3 H), 5.17 (m, 2 H), 5.87 (m, 1 H); ^{13}C NMR (δ, $CDCl_3$) 34.2, 43.1, 52.0, 116.7, 136.2, 141.8, 144.4, 161.4, 161.8; IR (cm^{-1}, $CHCl_3$) 3010, 2960, 2940, 1725, 1640, 1440, 1329, 1290, 1260, 1215; MS (CI) 197 (71%), 165 (100%), 137 (6%), 97 (12%), 85 (32%), 71 (46%); exact mass 196.0729 (obsd) 196.0735 (calcd for $C_{10}H_{12}O_4$).

Conversion of Dimethyl 3-Vinylcyclobutene-1,2-dicarboxylate to Dimethyl 1,4-Cyclohexadiene-1,2-dicarboxylate. A 72:28 mixture of the vinylcyclobutene and cyclohexadiene diesters (0.2225 g, 1.1 mmol), benzene (1.28 mL, 14.4 mmol), dimethylformamide (0.41 mL, 5.3 mmol), nickel tetracarbonyl (0.69 mL, 5.3 mmol), and dodecane (internal standard, 0.766 g, 0.4 mmol) were mixed in a three-necked flask under argon and the flask was immersed into an 80 °C oil bath. After 26 min, all of the vinylcyclobutene diester was converted to the cyclohexadiene diester as determined by gas chromotography. The reaction mixture was then cooled to room temperature and worked up in the usual manner to yield 0.0830 g (0.4 mmol, 36% yield) of the cyclohexadiene diester.

Control Experiment for the Conversion of Dimethyl 3-Vinylcyclobutene-1,2-dicarboxylate to Dimethyl 1,4-Cyclohexadiene-1,2-dicarboxylate. A 62:38 mixture of the vinylcyclobutene diesters (0.2288 g, 1.2 mmol), benzene (1.9 mL, 21.4 mmol), dimethyl formamide (0.4 mL, 5.2 mmol), and dodecane (internal standard, 0.0719 g, 0.4 mmol) were mixed in a three-necked flask under argon and the flask was immersed into an 80 °C oil bath. The reaction was monitored by gas chromotography for 3.5 h. The reaction was then allowed to cool to room temperature and worked up in the usual manner to yield 0.1145 g (0.6 mmol, 50% recovery) of the vinylcyclobutene/cyclohexadiene mixture. At t = 0, there are 0.72 mmol vinylcyclobutane and 0.44 mmol cyclohexadiene present. At t = 3.5 h, there are 0.05 mmoles vinylcyclobutene and 0.48 mmoles cyclohexadiene present.

Control Experiment for the Conversion of Dimethyl 3-Vinylcyclobutene-1,2-dicarboxylate to Dimethyl 1,4-Cyclohexadiene-1,2-dicarboxylate. A 76:24 mixture of the vinylcyclobutene and the cyclohexadiene diesters (0.03 g, 0.15 mmol), benzene (0.29 mL, 3.3 mmol), nickel tetracrabonyl (0.12 mL, 0.9 mmol), and dodecane (internal standard, 0.017 mL, 0.075 mmol) were mixed in a three-necked flask under argon, and the flask was immersed into an 80 °C oil bath. Within 30 min, all the vinylcyclobutene diester was converted to the cyclohexadiene diester as determined by gas chromotography. The reaction mixture was then cooled to room temperature and worked up in the usual manner to yield 0.01 g (0.05 mmol, 33% yield) of the cyclohexadiene diester.

Dimethyl 3-Vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate-d_{10}. This was synthesized in a manner analogous to the vinylcyclobutane-d_4, except that the anhydride was hydrolyzed with D_2O and the diacid was esterified with CD_2N_2. This material (0.178 g, 0.6451 mmol) was mixed with 0.164 g (0.616 mmol) of the d_0 material: MS (CI), 267 (100%), 268 (13%), 269 (66%), 271 (12%), 274 (6%), 275 (18%), 276 (26%), 277 (23%), 278 (16%), 279 (6%).

Ring Expansion of Dimethyl 3-Vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate-d_{10}. Using the above mixture of d_0 and d_{10} isomers, this reaction was performed in a manner analogous to that discussed previously: MS (CI); 197 (100%), 198 (12%), 199 (2%), 203 (5%), 204 (12%), 205 (20%), 206 (18%), 207 (9%), 208 (1%).

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