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Note

The rearrangement of 3-vinylcyclobutene derivatives promoted by metallic Lewis acids

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Abstract

The rearrangement of 3-vinylcyclobutene derivatives in the presence of metallic Lewis acids is discussed. Although most of the Lewis acids tried were too weak to cause any chemistry to occur, WCl_6 and $AlCl_3$ promote an interesting isomerization reaction. Especially significant is, for the first time, starting with a vinylcyclobutene, a product with a five-membered ring rather than a six-membered ring was obtained. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lewis acid; Rearrangement reaction

1. Introduction

Vinylcyclobutene (**1**) contains both an electron-rich and an electron-poor double bond. Recently, we have shown that upon reaction with an electron-rich metal complex, such as L_2NiBr [Ni(I)], $FeCl_2$ [Fe(II)], Cp_2TiCl [Ti(III)], $TiCl_3$ [Ti(III)] or SmI_2 [Sm(II)], all of which are oxidized easily by an inner sphere process, compound **1** isomerizes to give only a six-membered ring product. With Ni(I) and Fe(II), the product is cyclohexadiene (**2**); with Ti(III) and Sm(II), the product is phthalate (**3**). When cyclohexadiene (**2**) is treated with Ti(III) or Sm(II), it aromatizes to give **3**. We believe that the first step in the isomerization reaction is an electron transfer to the electron-poor double bond [1,2] (Scheme 1).

In contrast, **1** is stable upon reaction with the (electron-poor) Lewis acid metal complexes L_2NiBr_2, $FeCl_3$, Cp_2TiCl_2, $ZnCl_2$ and $SmCl_3$. This seemed strange to us, given the fact that, as mentioned above, **1**, and especially **1b**, has an electron-rich double bond with which a Lewis acid could react. In an attempt to find a Lewis acid metal complex that would react with compound **1**, and thus be able to compare this chemistry to that with the electron-donating metal complexes mentioned above, we have studied the reaction of compound **1b** with a large number of different metal complexes. For many of the complexes tried, starting material **1b** was recovered in high yield. In a few cases, intractable material was obtained. In this manuscript, we compare the results from using titanium and zirconium. More importantly, we report the results from using the Lewis acids $AlCl_3$ and WCl_6, because they caused an interesting and new isomerization reaction to occur. Specifically, for the first time, we obtained a product with a five-membered ring rather than a six-membered ring.

2. Results and discussion

2.1. Background

All of the reactions using a Lewis acid were performed at room temperature because when **1b** is heated to 80 °C for 72 h, a thermal rearrangement occurs to give **5** (Scheme 2). The reaction most likely proceeds by a ring-opening of **1b** to give **4**, followed by a ring-closure to give **5** [3]. In a control experiment to insure that any chemistry we observed was due to the Lewis acid and not a Bronsted acid, we discovered that compound **1b** is stable in the presence of dilute HCl for an extended period of time.

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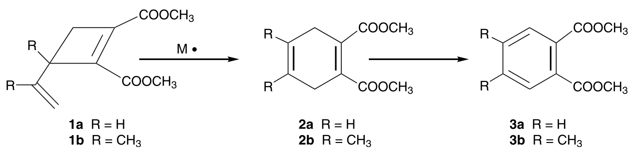
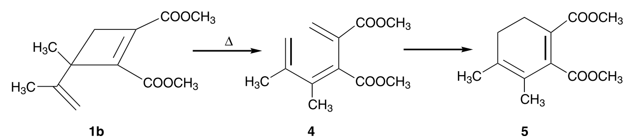
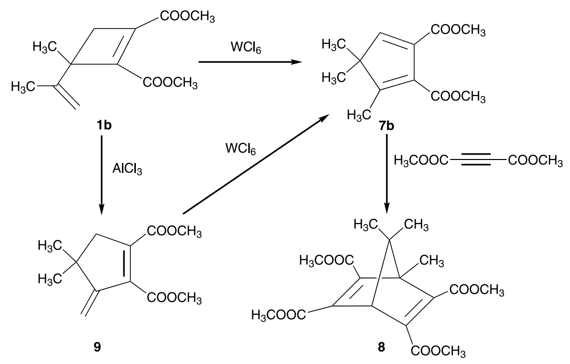


Scheme 1.



Scheme 2.



Scheme 4.

2.2. Titanium and zirconium

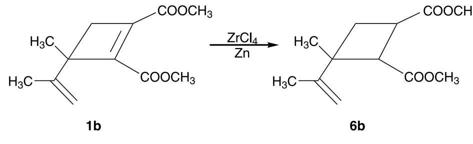
Previously, we found that vinylcyclobutene (**1b**) was stable in the presence of Cp_2TiCl_2. Not surprisingly, because it is a weaker Lewis acid, we have now found that **1b** is stable in the presence of Cp_2ZrCl_2. Moving to the stronger Lewis acid $TiCl_4$, here compound **1b** only forms intractable material. We found no evidence for any type of isomerization reaction. We next decided to try the somewhat weaker Lewis acid $ZrCl_4$; however, **1b** did not react under these reaction conditions [4].

As an aside, because $TiCl_3$ caused the rearrangement of **1b** to **3b** mentioned in the Introduction, we wanted to learn the effect of $ZrCl_3$, which is readily made from the reaction of $ZrCl_4$ and activated zinc. As shown in Scheme 3, the mixture of $ZrCl_4$ and Zn reduces the electron-poor double of **1b** to give **6b** in very high yield. This is one of the few cases of an easy reduction of an electron-poor double bond [5].

The ring strain of the four membered ring is not needed for this reaction to occur. We found that the $ZrCl_4$/Zn mixture will reduce dimethyl maleate to dimethyl succinate in nearly quantitative yield. One of the control experiments we did was to treat **1b** with a mixture of Zn with a small amount of concentrated HCl. This reaction also gave exclusively **6b** in quantitative yield. Thus, the $ZrCl_4$ must be acting as a source of HCl and not as the actual hydrogenation catalyst.

2.3. WCl_6 and $AlCl_3$

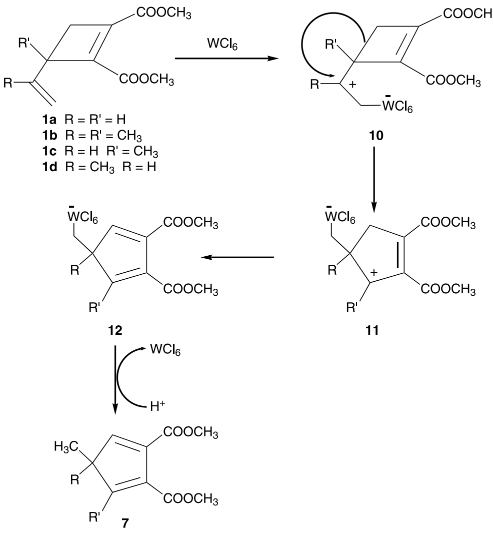
In contrast to the zirconium and titanium complexes, the Lewis acid WCl_6 isomerizes compound **1b** (Scheme 4), but in an entirely different manner from that observed previously with the electron-donating metal complexes. In this case, the product, **7b**, has a five-membered ring and not a six-membered ring. Compound **7b** was identified spectroscopically, and by the fact that it readily undergoes a Diels–Alder reaction with dimethyl acetylenedicarboxylate to give symmetrical compound **8**.



Scheme 3.

When **1b** was stirred with $AlCl_3$, a small amount of **7b** and mainly isomeric compound **9** were formed. Compound **9** was identified spectroscopically and by the fact that it is stable in the presence of dimethyl acetylenedicarboxylate. Compound **9** isomerizes to compound **7b** in the presence of WCl_6; compound **7b** is stable in the presence of $AlCl_3$. Although vinylcyclopropenes are known to give five-membered ring products [6], to the best of our knowledge, these are the first examples of a vinylcyclobutene rearranging to generate a product that contains a five-membered ring.

In an attempt to understand the mechanism of this rearrangement, compound **1a** ($R = R' = H$), compound **1c** ($R = H$ and $R' = CH_3$), or compound **1d** ($R = CH_3$ and $R' = H$) and WCl_6 were reacted (Scheme 5). Unlike the radical chemistry shown in Scheme 1, in which compounds **1a** and **1b** react very similarly, with WCl_6,



Scheme 5.

compound **1a** is stable. Compound **1a** also is stable upon reaction with $AlCl_3$.

Due the nature of our synthesis of compound **1**, only a mixture of **1c** and **1d** could be obtained. Unfortunately, we found that although these compounds could be separated on a small scale to obtain spectroscopic data, they could not be separated on a larger scale to study their chemistry. Thus, a mixture of **1c** and **1d** was allowed to react with WCl_6 using the same reaction conditions as were used with **1a** and **1b**. At the end of the reaction, isomer **1c**, which has the methyl group only on the ring, was unchanged. Isomer **1d**, which has the methyl group only on the vinyl double bond, isomerized to **7d**, but in a much lower yield than the isomerization of **1b**.

Based on these results, we propose the mechanism shown in Scheme 5, in which WCl_6 adds to the vinyl group only if the resulting cation is stabilized by a methyl group (i.e. $R = CH_3$), the five-membered ring is generated by a Wagner–Meerwein shift of the C3–C4 bond of the vinylcyclobutene, and then the Lewis acid is lost to give the product [7]. The rearrangement takes place with $R' = CH_3$ or with $R' = H$, probably due to the relief of strain of the four-membered ring; however, it is much more efficient when $R' = CH_3$ because the resulting cation in intermediate **11** is stabilized by a methyl group. The breaking of the C3–C4 bond here is in contrast to Scheme 1 in which the C3–C4 bond is stable and the net result is breaking the C2–C3 bond. If it were the C2–C3 bond that broke here, we would not have obtained product **7b**, but rather an isomer.

3. Conclusion

Thus, metal complexes that are easily oxidized transfer an electron to the electron-poor double bond of the ring and a radical rearrangement, as shown in Scheme 1, occurs to give a six-membered ring product. Metal complexes that are Lewis acids of intermediate strength coordinate to the more electron-rich vinyl group, and if a methyl is present to stabilize the carbocation, a Wagner–Meerwein shift occurs to give a five-membered ring product (Scheme 5).

4. Experimental

All experiments were carried out under an argon atmosphere in glassware that was base-washed and oven-dried. THF and dioxane were distilled from potassium and degassed with argon prior to use. Deionized water was purged with argon for 10 min prior to use. Compound **1** was synthesized as discussed previously [1,2]; however, the dechlorination reaction was improved and the results are reported below. All NMR spectra were recorded on a 250-MHz spectrometer with $CDCl_3$ as the solvent and with added TMS at 0.00 ppm. IR spectra were recorded on an FTIR spectrophotometer using a KBr cell with a path length of 0.05 mm and CCl_4 as the solvent. Mass spectra were measured on a GC/MS instrument using an SPB-1 capillary column and electron impact ionization. The initial injection temperature was 80 °C; the temperature was then raised to 250 °C at 10 °C per min and then held at 250 °C for 10 min. The injector temperature was kept at 175 °C and the detector temperature was 250 °C. High-resolution mass spectra were obtained either using electrospray or electron impact. Routine GC analyses were performed with a packed column and an FID detector. Column: 5% SP 2100 on 100/120 Supelcoport, 10′X1/8″; carrier: He, 33 ml min^{-1}; the rearrangement reactions were monitored using column: 5% FFAP, Chromosorb W-HP 100/120, 3′X1/8″; carrier: He, 30 ml min^{-1}.

4.1. *Preparation of Riecke zinc [8]*

Potassium metal (1.00 g, 25.6 mmol) was placed in a 100-ml three-neck round-bottom flask. THF (20 ml) was added and the mixture was heated to reflux. $ZnCl_2$ (1.69 g, 13.0 mmol) was dissolved in 20 ml of THF and placed in a dropping funnel. The $ZnCl_2$ solution was added dropwise to the vigorously stirred suspension over a period of 30 min. A black mixture of finely dispersed Riecke Zn was formed with a concentration of 0.32 mmol ml^{-1}. The Riecke Zn could be stored as a suspension under argon for several days.

4.2. *Dechlorination to give compound **1b***

The reaction was run in a 50-ml round-bottom flask sealed with a septum. A 25-ml screw cap test tube, suitable for use in a centrifuge, was used to activate the zinc. The test tube was equipped with a magnetic stir bar and purged with argon. Zinc dust and granulated zinc (500 mg, 8 mmol of each) were added and mixed. Two milliliters of 10% H_2SO_4 were added to the tube and the mixture was stirred vigorously for 5 min. Adding a few drops of ether to the mixture prevented foaming. The zinc formed a gray spongy mass that rose to the surface. The acid was removed with a pipette and the activated zinc was washed two times with 1 ml of water. Then 1 ml of water was added, and the Riecke Zn suspension (approximately 200 μl) was added to the resulting suspension until the zinc turned dark gray. The change of color indicated that all of the remaining acid and other impurities were consumed, and there was a small amount of Riecke Zn in the reaction mixture. The test tube was sealed, put into a centrifuge, which removed most of the water. The residual water was removed by washing the activated zinc three times with 1 ml of dioxane, and finally, the active metal was suspended in 2 ml of dioxane. The dichloro-precursor to compound **1b** (500 mg, 2 mmol) was dissolved in 25 ml of hexane and placed in a round bottom flask. To the flask was added a magnetic stirring bar, and argon was passed into the solution with a pipette for 10 min. The zinc suspension was added to the solution and the flask was sealed with a septum. The reaction mixture was stirred for 24 h at room temperature (r.t.). A change of color to light gray and the formation of very fine particles in the suspension indicated that the dechlorination had taken place. GC analysis showed that there was no starting material left. Upon standing, the remaining solid settled and the colorless solution could be removed by with a pipette. The residue was then placed in a centrifuge to recover the remaining solution. Removal of the solvent under vacuum yielded the crude product as a colorless oil. The product was distilled using a short-path condenser at 0.5 mmHg to give 303 mg (1.35 mmol, 69% yield). Compounds **1a**, **1c** and **1d** were synthesized in a similar manner. Spectroscopic data for compound **1** were reported previously [1,2].

4.3. Thermal rearrangement of compound *1b*

Compound **1b** (125 mg, 0.56 mmol) was placed in a centrifuge tube, dissolved in 6 ml of dioxane, and heated to 80 °C under argon for 72 h. The solvent was removed under vacuum, and the residue was distilled at 100 °C using a Kugelrohr to give 114 mg (0.51 mmol, 91% yield) of colorless oil of **5**. ^{1}H-NMR: δ: 1.72 (s, 3H), 1.87 (s, 3H), 2.20 (t, $J = 10$ Hz, 2H), 2.45 (t, $J = 10$ Hz, 2H), 3.74 (s, 3H), 3.86 (s, 3H). ^{13}C-NMR: δ: 20.09, 21.90, 27.45, 30.42, 51.95, 52.05, 121.98, 122.85, 139.8, 143.90, 167.02, 170.50. IR (CCl_4): 2950 (w), 1741 (s), 1581 (w), 1435 (m), 1272 (s), 1228 (m), 1194 (w), 1138 (m), 1041 (w) cm^{-1}. MS (m/z): 224 (19%), 192 (100%), 177 (62%), 149 (12%), 133 (50%), 105 (93%), 91 (65%), 77 (44%), 59 (46%). TOF MS ES+: exp. 247.0941, calculated for $C_{12}H_{16}NaO_4^+$ 247.0922.

4.4. Reduction of *1b* with zinc and catalytic $ZrCl_4$

Zinc was activated as discussed above in the dechlorination experiment. Compound **1b** (50 mg, 0.2 mmol) in 2 ml of dioxane was added to the zinc. The mixture was stirred under argon and $ZrCl_4$ (5 mg, 0.02 mmol) was added. The tube was sealed and the mixture was stirred at r.t. overnight. The suspension turned from gray to white indicating the consumption of zinc. The dioxane solution was removed using a centrifuge. After concentrating under vacuum, a colorless oil of **6b** was obtained in nearly quantitative yield. ^{1}H-NMR: δ: 1.19 (s, 3H), 1.72 (s, 3H), 2.01 (m, 1H), 2.22 (m, 1H), 3.47 (m, 2H), 3.70 (s, 6H), 4.84 (s, 2H). ^{13}C-NMR: δ: 17.76, 19.75, 21.56, 33.37, 33.76, 34.01, 44.31, 48.22, 51.39, 51.48, 51.69, 109.11, 111.47, 151.00, 171.72, 174.08. IR (CCl_4): 2952 (m), 1737 (s), 1645 (w), 1436 (m), 1375 (m), 1324 (m), 1235 (s), 1218 (s), 1174 (s), 1029 (m), 897 (m) cm^{-1}. MS (m/z): 194 (2%), 166 (30%), 107 (100%), 91 (28%), 82 (47%), 67 (64%), 59 (24%). TOF MS ES+, exp. 249.1079, calculated for $C_{12}H_{18}NaO_4^+$ 249.1097.

4.4.1. Rearrangement of compound *1b* with WCl_6

Compound **1b** (100 mg, 0.5 mmol) was dissolved in 3 ml of dioxane and placed in a 15-ml screw cap test tube. The solution was purged with argon for 5 min, then WCl_6 (176 mg, 0.45 mmol) was added, the tube was sealed, and the reaction mixture was stirred at room temperature for 72 h. During this time a bright blue precipitate formed. After removing the solid using a centrifuge, the mixture was filtered over silica gel and concentrated. The crude product was purified by column chromatography to give 28 mg (0.13 mmol, 28% yield) of colorless oil of **7b**. ^{1}H-NMR: δ: 1.14 (s, 6H), 2.00 (s, 3H), 3.78 (s, 3H), 3.81 (s, 3H), 6.83 (s, 1H). ^{13}C-NMR: δ: 11.01, 20.89, 51.48, 51.64, 53.92, 127.09, 133.16, 150.80, 160.63, 164.72, 165.73. IR (CCl_4): 2970 (w), 2953 (w), 2258 (w), 1721 (s), 1576 (w), 1439 (m), 1364 (w), 1316 (w), 1287 (m), 1239 (m), 1209 (m), 1118 (w), 1066 (w), 1021(w) cm^{-1}. MS (m/z): 224 (11%), 192 (18%), 177 (19%), 164 (100%), 133 (78%), 105 (42%), 91 (42%), 77 (20%), 59 (20%). HRMS: exp. 224.1029, calculated for $C_{12}H_{16}O_4$ 224.1049.

4.5. Rearrangement of *1b* with $AlCl_3$

A solution of 100 mg (0.5 mmol) **1b** in 3 ml dioxane was placed in a test tube. The solution was purged with argon for 5 min. $AlCl_3$ (59 mg, 0.45 mmol) was added and the tube was sealed under argon. At the beginning, the solution was clear and colorless. After stirring overnight, a white–blue precipitate formed. After stirring at r.t. for 72 h, the solid was removed using a centrifuge, and the solution was concentrated under vacuum. GC analysis showed the formation of two products in a 3:1 ratio, which were separated by column chromatography. The major product was identified as the *exo*-methylene compound **9** (34 mg, 0.15 mmol, 34% yield) and the minor as **7b** (17 mg, 0.076 mmol, 17% yield). Spectral data for **9**: ^{1}H-NMR: δ: 1.19 (s, 6H), 2.62 (s, 2H), 3.77 (s, 3H), 3.87 (s, 3H), 5.08 (s, 1H), 5.19 (s, 1H). ^{13}C-NMR: δ: 29.33, 41.14, 47.04, 52.00, 52.23, 53.37, 108.98, 135.60, 144.20, 159.80, 164.63. IR (CCl_4): 2955 (m), 2258 (w), 1716 (s), 1618 (m), 1438 (m), 1354 (m), 1285 (s), 1228 (s), 1126 (m), 1058 (m) cm^{-1}. MS (m/z): 224 (51%), 193 (59%), 177 (90%), 164 (52%), 133 (72%), 119 (39%), 105 (100%), 91 (79%), 77 (49%), 59 (58%). HRMS: exp. 224.1070, calculated for $C_{12}H_{16}O_4$ 224.1049.

4.6. Reaction of **7b** with dimethyl acetylenedicarboxylate

Compound **7b** (30 mg, 0.1 mmol) was dissolved in 1 ml of dioxane and placed in a test tube. The solution was purged with argon for 5 min. Then, dimethyl acetylenedicarboxylate (100 mg, 0.7 mmol) was added, and the mixture was stirred for 1 min. The tube was sealed under argon and placed on top of a GC to maintain an average temperature of 35 °C. After 1 week, the solution was concentrated under vacuum and purified by column chromatography using silica gel. The purified product crystallized upon standing to give fine white needles with a melting point of 38 °C (29 mg, 0.078 mmol, 78%). ^{1}H NMR: δ: 1.15 (s, 6H), 1.24 (s, 1H), 3.76 (s, 6H), 3.84 (s, 6H). MS (m/z): 335 (9%), 307 (69%), 293 (100%), 275 (64%), 243 (35%), 184 (26%), 115 (30%), 73 (90%), 59 (41%).

4.7. Reaction of **1c** and **1d** with WCl_6

A 70:30 mixture, as determined by GC analysis using an internal standard, of **1c** and **1d** (200 mg, 1 mmol) was dissolved in 6 ml of dioxane and WCl_6 (374 mg, 0.95 mmol) was added. The mixture was stirred at r.t. for 72 h. At that time, as determined by GC/MS, the concentration of starting material **1c** had not changed, the concentration of **1d** decreased, and a small amount of **7d** was detected. MS data for **9d**: 210 (10%), 178 (45%), 163 (18%), 152 (22%), 119 (35%), 105 (18%), 91 (100%), 77 (30%), 59 (49%).

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