Synthesis of Vinyl Chlorides *via* Triphosgene-Pyridine Activation of Ketones

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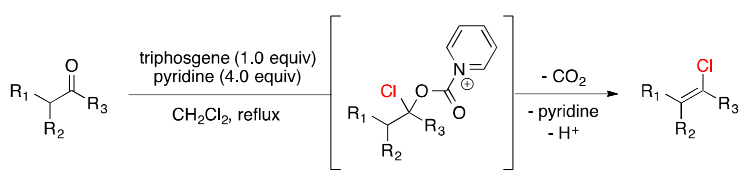
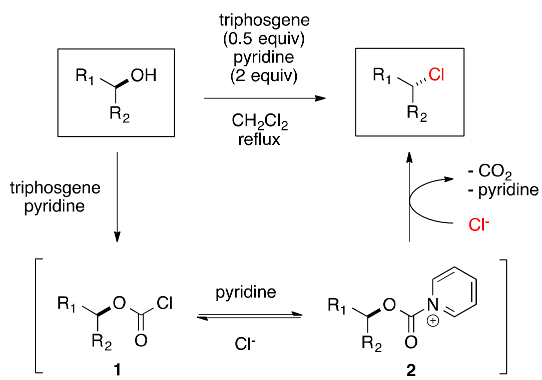
ABSTRACT



Herein we describe a mild method to prepare aliphatic and aromatic vinyl chlorides from their corresponding ketones via triphosgene-pyridine activation in dichloromethane at reflux. The mechanism of this reaction is proposed to involve formation of a putative α-chloro pyridinium carbamate intermediate, which appeared to readily undergo an E2 elimination in the presence of pyridine.

Vinyl chlorides are a ubiquitous functional group. They are readily found in numerous chlorine-containing natural products.[1] Furthermore, vinyl chlorides play a significant role in organic synthesis, as they serve as a convenient intermediate for transition metal-catalyzed carbon-carbon and carbon-heteroatom bond forming processes.[2] Naturally, syntheses of vinyl chlorides have been subjected to multiple studies because of their broad applications. In fact, there are abundant precedents on the production of vinyl chlorides from a variety of starting materials, including α,β-unsaturated carbonyl compounds,[3] vinyl trifluoroborates,[4] vinyl triflates,[5] alkynes,[6] and cyclopropenes.[7] Preparation of vinyl chlorides could be also expediently carried out from ketones. Nevertheless, there are many challenges often associated with this approach. For example, many of the established protocols often used strongly acidic conditions[8] or harsh halogenating reagents, such as thionyl chloride and other chlorinated phosphorous-based reagents (PCl_3, PCl_5, $POCl_3$).[9] These sets of reaction conditions thereby limited the scope of substrates.[10] There are also reports on methods that generated byproducts, including contamination of *geminal*-dichloride adducts that were often inseparable by chromatography from the desired vinyl chlorides.[11]

Driven by our synthetic interests in chlorosulfolipid natural products,[12] we recently developed a series of new reactions that enabled robust conversion of unreactive aliphatic alcohols to the corresponding alkyl chlorides under exceedingly mild conditions.[13] For instance, as shown in Scheme 1, we discovered that treatment of secondary alcohols with triphosgene and pyridine in dichloromethane at reflux cleanly produced the corresponding alkyl chlorides with excellent stereospecificity.[13a] Our chemistry was operationally simple; the existence of triphosgene as a stable non-hygroscopic crystalline material at room temperature permitted easy and safe handling of the chlorinating reagent.[14] In fact, this reaction did not require scrupulously inert nor anhydrous conditions. More importantly, our chlorination method was high yielding and advantageously tolerated by a variety of sensitive functionalities that otherwise would be problematic under classical chlorination conditions.[13b] The mechanism of this reaction was proposed to involve conversion of the starting alcohol to pyridinium carbamate **2** via chloroformate **1**, upon treatment with triphosgene and pyridine. This novel mode of nucleophilic activation subsequently enhanced the electrophilicity of intermediate **2** at the carboxyl position, specifically towards an S_N2 nucleophilic substitution by chloride ions, which ultimately led to an inversion of stereochemistry. This process also regenerated the nucleophilic promoter, *i.e.* pyridine, and carbon dioxide as the sole byproduct.

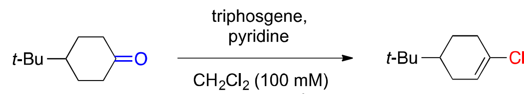


Scheme 1. Triphosgene-Pyridine Promoted Stereospecific Chlorination of Alcohols

These studies naturally inspired us to investigate the applicability of our chlorination conditions to convert ketones to their corresponding chlorinated products, such as vinyl chlorides. Literature examples on the utility of triphosgene to activate ketones are quite rare. One such example was reported by Su and a co-worker, in which they synthesized vinyl chlorides by subjecting ketones to a mixture of catalytic $Sc(OTf)_3$-DMF-benzoyl chloride in the presence of triphosgene.[11a] Herein, we wish to report our metal-free variant to this chemistry, highlighted by a convenient and practical use of triphosgene and pyridine under mild conditions to achieve this useful functional group interconversion.

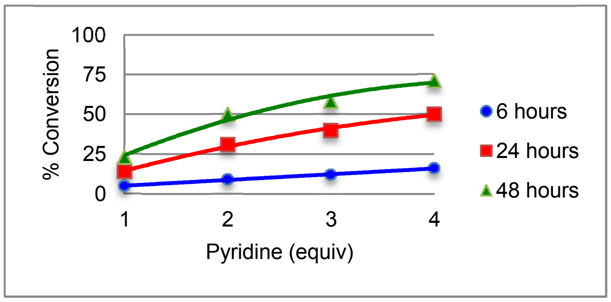
Our preliminary studies are depicted in Figure 1, in which 4-*tert*-butyl cyclohexanone **3** was employed as the starting material. As shown in Graph 1A, these studies were initially carried out by varying the amount of pyridine by 1.0 equivalent increments while employing a constant 0.5 equivalent of triphosgene. These reactions were performed at room temperature as a 100 mM solution in dichloromethane based on starting ketone **3**. The progress of reaction was then periodically monitored by GC analyses. Gratifyingly, these pilot conditions readily generated the corresponding vinyl chloride **4**. We observed that the extent of product formation appeared to be directly correlated to the amount of pyridine introduced to the solution, but the starting ketone was not fully consumed under these conditions even after 48 hours of stirring. Interestingly, an attempt to activate ketone **3** with triphosgene and pyridine in non-chlorinated solvents failed to yield the desired vinyl chloride. In addition, the use of other chlorinated solvents, such as chloroform and dichloroethane, only resulted in lower conversion yields.

Figure 1. Reaction Optimization[a,b]

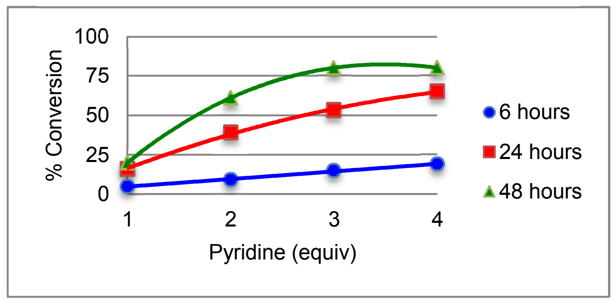


3 → 4

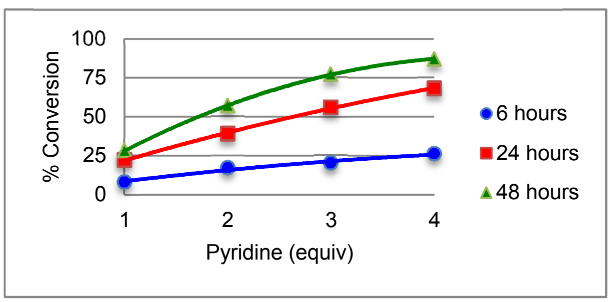
Graph 1A.
Conditions: triphosgene (0.5 equiv), pyridine (n equiv), room temperature



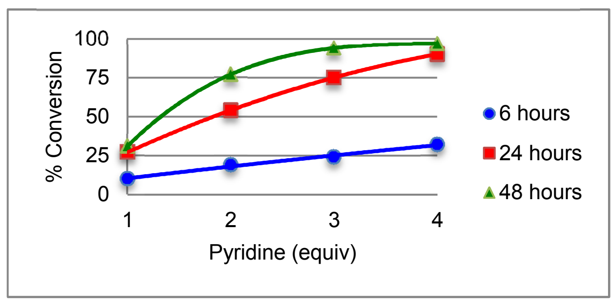
Graph 1B.
Conditions: triphosgene (0.5 equiv), pyridine (n equiv), reflux



Graph 1C.
Conditions: triphosgene (1.0 equiv), pyridine (n equiv), room temperature



Graph 1D.
Conditions: triphosgene (1.0 equiv), pyridine (n equiv), reflux



(a) Yields were determined by GC analyses of the crude mixtures assuming that the starting material and product elicited identical GC responses.

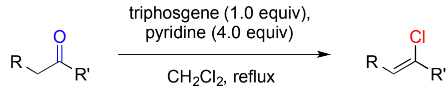
(b) The remaining material in the crude mixture was unreacted starting ketone **3**.

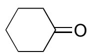
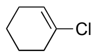
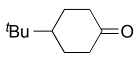
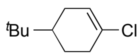
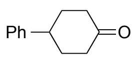
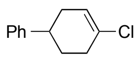
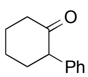
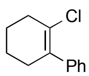
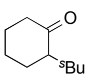
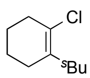
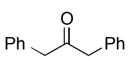
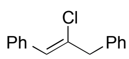
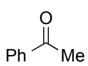
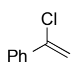
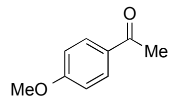
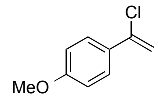
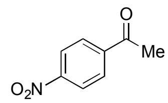
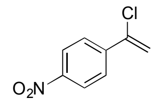
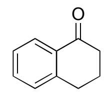
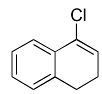
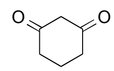
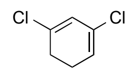
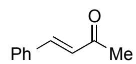
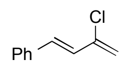
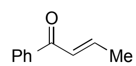
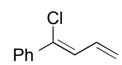
To help push the reaction to reach completion, the above experiments were repeated at reflux (Graph 1B). Similarly, the reaction appeared to plateau at 80% conversion with 4.0 equivalents of pyridine. As shown in Graphs 1C and 1D, we then increased the amount of triphosgene to 1.0 equivalent while steadily modulating the amount of pyridine from 1.0 to 4.0 equivalents. This new set of reactions were also conducted both at room temperature and reflux.

Eventually, the use of 4.0 equivalents of pyridine at reflux was found to yield the highest production of vinyl chloride **4** (up to 97% GC conversion) after 48 hours of reaction.

Overall, the optimal reaction conditions were established to involve the use of 1.0 equivalent of triphosgene and 4.0 equivalents of pyridine in dichloromethane at reflux. We then evaluated the compatibility of various ketones in this methodology. To expedite the rate of reaction, the scope of substrate study was performed in preparative scales at 200 mM concentration for aliphatic ketones or 500 mM for aromatic ketones. As shown in Table 1, entries 1-5, various cyclohexanone-derived substrates were initially subjected to the chlorination conditions. Simple cyclohexanone cleanly produced the corresponding vinyl chloride **6a** in 100% GC conversion. However, an attempt to purify this product only led to 20% isolation yield presumably due to its rapid decomposition during column chromatography. The use of 4-*tert*-butylcyclohexanone and 4-phenylcyclohexanone generated vinyl chlorides **6b** and **6c**, respectively, in quantitative GC yields and good isolation yields. Exposure of 2-phenylcyclohexanone and 2-*sec*-butylcyclohexanones to these chlorination conditions furnished vinyl chlorides **6d** and **6e** as a mixture of regioisomers, favoring the fully substituted double bond. Interestingly, starting materials **5d** and **5e** was not fully consumed after 24 hours of stirring. Similarly, the apparent instability of vinyl chlorides **6d** and **6e** towards chromatographic purification resulted in reduced isolation yields.

Table 1. Scope of Substrates



entry	substrate	product(s)	GC Yield[a,b]	Isolation Yield[c]	time (h)
1[d]	 5a	 6a	100%	20%	16
2[d]	 5b	 6b	100%	80%	15
3[d]	 5c	 6c	100%	93%	24
4[d]	 5d	 6d	85% (3:1 rr)	42%	24
5[d]	 5e	 6e	66% (6:1 rr)	34%	24
6[e]	 5f	 6f	43% (5:1 *Z*:*E*)	23% (5:1 *Z*:*E*)[f]	72
7[e]	 5g	 6g	71%	33%	48
8[e]	 5h	 6h	89%	22%	48
9[e]	 5i	 6i	51%[g]	54%[h]	72
10[e]	 5j	 6j	98%	54%	24
11[d]	 5k	 6k	79%	41%	24
12[e]	 5l	 6l	100%	25%	24
13[e]	 5m	 6m	trace[i]	--	24

(a) Yields were determined by GC-MS analyses of the crude mixtures assuming that the starting material and product elicited identical GC responses.

(b) The remaining material in the crude mixture was unreacted starting ketone.

(c) Low isolation yields were presumably due to decomposition of vinyl chlorides during chromatography. We screened a variety of chromatographic conditions, including the use of neutralized silica and alumina.

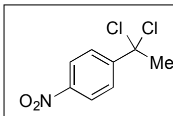
(d) Reactions were performed at 200 mM concentration based on starting ketones.

(e) Reactions were performed at 500 mM concentration based on starting ketones.

(f) The olefin isomers were inseparable by chromatography. The E:Z ratio was determined by ^{1}H NMR. The major olefin geometry was determined by an NOE experiment.

(g) The GC-MS analysis of the crude material indicated 10% of *geminal*-dichloride byproduct **7**.

(h) The combined yield for an inseparable 5:1 mixture of vinyl chloride **6i** and *geminal*-dichloride byproduct **7**.



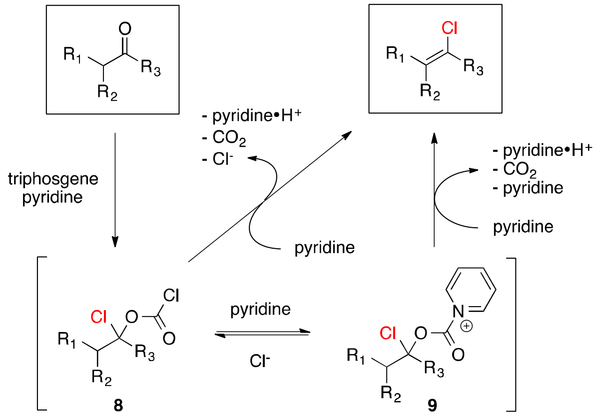
7

(i) Decomposition of starting material was observed.

While cyclic ketones appeared to be more readily tolerated in this methodology, acyclic aliphatic ketone, such as dibenzylketone **5f**, was surprisingly rather problematic. Treatment of this compound to the established triphosgene-pyridine activation led to formation of vinyl chloride **6f** in modest 43% conversion even though the reaction was performed at an increased concentration for an extended period of time. In addition, the GC analysis of the crude material revealed a 5:1 mixture of olefin isomers, favoring the *Z* geometry. As demonstrated in entries 7-9, the compatibility of various aromatic ketones was also investigated through the use of substituted acetophenones **5g-5i**. Similarly, the corresponding vinyl chlorides **6g-6i** were produced in a varying degree of conversion and isolation yields, depending upon the stability of the products during chromatography. Unexpectedly, *para*-nitroacetophenone generated *geminal*-dichloride adduct **7** in 10% yield. This byproduct was inseparable by chromatography from the desired vinyl chloride **6i**. We also subjected 1-tetralone **5j** to this reaction, and this compound furnished the corresponding product **6j** in good conversion and isolation yields. As shown in entries 11-13, the use of more elaborate substrates, such as cyclohexane-1,3-dione **5k**, readily produced the corresponding *bis*(vinyl chloride) **6k** in a decent yield. Furthermore, exposure of α,β-unsaturated ketone **5l** to these chlorination conditions afforded the desired divinyl chloride

6l in 100% conversion, but the apparent instability of this compound under chromatography again rendered a low isolation yield. Interestingly, α,β-unsaturated ketone **5m** was not reactive under identical chlorination conditions. In fact, this starting material only produced a trace amount of divinyl chloride **6m**, along with other unidentifiable decomposition materials.

The mechanism for our vinyl chloride formation is proposed in Scheme 2. We believed that activation of ketones with triphosgene and pyridine in dichloromethane initially produced α-chloro chloroformate **8**. Although this presumed intermediate was not observed in any of our GC-MS and NMR studies, the potential participation of this species was supported by Coghlan's report, which described the conversion of aldehydes to analogous α-chloro chloroformate functionality under similar reaction conditions.[15] As depicted in Figure 1, the extent of vinyl chloride formation appeared to be dependent on the concentration of pyridine. This could hypothetically suggest the involvement of pyridine as a nucleophilic activator, which transformed α-chloro chloroformate **8** to the corresponding α-chloro pyridinium carbamate intermediate **9**.[13a] Such a putative reactive intermediate then proceeded to undergo an E2 elimination of the pyridinium carbamate moiety upon deprotonation of the adjacent α-hydrogen, presumably by pyridine. This process would eventually produce the corresponding vinyl chloride while regenerating pyridine and releasing carbon dioxide as a byproduct. Nevertheless, at this point, we could not rule out an alternative pathway, which involved the possibility of α-chloro chloroformate **8** to undergo direct E2 elimination induced by pyridine.



Scheme 2. Proposed Reaction Mechanism

CONCLUSION

We have demonstrated that ketones could be conveniently transformed to vinyl chlorides, using a simple protocol with a mixture of triphosgene and pyridine in dichloromethane at reflux. Although our method is proven to be mild and applicable for various types of ketones, the presumed instability of the desired vinyl chloride products under chromatography rendered their isolation rather difficult. Nonetheless, our investigations have shed a new insight into a novel activation of α-chloro chloroformates by pyridine to α-chloro pyridinium carbamate intermediates.

EXPERIMENTAL SECTION

All materials, unless otherwise stated, were purchased from commercial sources and utilized without further purification. Anhydrous reactions were conducted in oven-dried glassware, which was then cooled under vacuum and purged with nitrogen gas. Anhydrous solvents (dichloromethane, toluene, acetonitrile, diethyl ether, and tetrahydrofuran) were filtered through activated 3Å molecular sieves under nitrogen in a solvent purification system. Reactions were either monitored by analytical thin layer chromatography (TLC Silica Gel 60 F_{254}, Glass Plates) and analyzed using 254 nm UV light and anisaldehyde – sulfuric acid or potassium permanganate stains, or via Gas Chromatography – Mass Spectrometry (GC-MS). The column for the GC-MS system was 5% phenyl methyl siloxane, measuring 30 meters in length with an internal diameter of 250 μm and film thickness of 0.25 μm. Low and high mass readings were set to 40 to 800 m/z, respectively. Oven, inlet, and detector temperatures were set to 250ºC, and helium was used as the inert carrier gas. Column chromatography was completed using silica gel or neutral alumina. Unless otherwise noted, all ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Chemical shifts (δ) are reported in ppm relative to residual $CHCl_3$ as an internal reference (^{1}H: 7.26 ppm, ^{13}C: 77.00 ppm). Coupling constants (*J*) are reported in Hertz (Hz). Peak multiplicity is indicate as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), x (septet), h (heptet), b (broad), and m (multiplet). FT-IR spectra were recorded using thin film, and absorption frequencies were reported in reciprocal centimeters (cm^{-1}). High Resolution Mass Spectrometry (HRMS) analyses were performed using Electron Spray Ionization – Time of Flight (ESI-TOF) method.

General Procedure. Into an oven-dried pressure vessel, ketone (1.0 equiv) was dissolved in anhydrous CH_2Cl_2 (200 mM or 500 mM concentration). Triphosgene (1.0 equiv) was added in one portion, followed by pyridine (4.0 equiv). The mixture was then warmed to a gentle reflux at 35°C bath, and the progress of reaction was monitored by GC-MS analyses. Upon completion, unless otherwise noted, the crude mixture was partition with 1M HCl and CH_2Cl_2 (1:1 ratio, 20 mL). The aqueous layer was further extracted with CH_2Cl_2 (3x10 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under vacuum. The resulting residue was then purified by flash column chromatography.

1-chloro-cyclohexene (6a).[16] Ketone **5a** (208 µL, 2.00 mmol) was dissolved in CH_2Cl_2 (10.0 mL) along with triphosgene (593 mg, 2.00 mmol) and pyridine (647 µL, 8.00 mmol). Without aqueous workup, the crude mixture was directly purified with column chromatography on neutral alumina using 100% pentane to afford vinyl chloride **6a** (47 mg, 0.40 mmol) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 5.79-5.78 (m, 1H), 2.30-2.25 (m, 2H), 2.10-2.05 (m, 2H), 1.75-1.69 (m, 2H), 1.60-1.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 131.9, 124.5, 32.8, 26.1, 23.7, 21.3. IR (cm^{-1}) = 2917, 2849, 2045, 1463, 995, 700. GC-MS: Rt = 7.55 min; M^+ = 116.0 calculated for C_6H_9Cl, experimental = 116.1.

4-*tert*-butyl-1-chloro-cyclohexene (6b).[11b] Ketone **5b** (309 mg, 2.00 mmol) was dissolved in CH_2Cl_2 (10.0 mL) along with triphosgene (593 mg, 2.00 mmol) and pyridine (647 µL, 8.00 mmol). After aqueous workup, the crude mixture was purified with column chromatography on silica gel using 100% hexanes to afford vinyl chloride **6b** (276 mg, 1.60 mmol) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 5.77 (t, J = 3.1 Hz, 1H), 2.40-2.26 (m, 2H), 2.10 (m, 1H), 1.90-1.82 (m, 2H), 1.39-1.24 (m, 2H), 0.87 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 131.6, 124.6, 43.0, 34.0, 32.1, 27.6, 27.2, 25.1. IR (cm^{-1}) =2959, 2868, 1366, 1025, 982, 719. GC-MS: Rt = 13.00 min; M^+ = 172.1 calculated for $C_{10}H_{17}Cl$, experimental = 172.1.

4-phenyl-1-chloro-cyclohexene (6c).[17] Ketone **5c** (261 mg, 1.50 mmol) was dissolved in CH_2Cl_2 (7.5 mL) along with triphosgene (445 mg, 1.50 mmol) and pyridine (485 µL, 6.00 mmol). After aqueous workup, the crude mixture was purified with column chromatography on silica gel using 100:0 → 98:2 → 96:4 hexanes : EtOAc to afford vinyl chloride **6c** (267 mg, 1.39 mmol) as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.38 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 3H), 5.95 (t, *J* = 3.0 Hz, 1H), 2.88 (m, 1H), 2.59 (m, 1H), 2.45 (dd, *J* = 5.5 Hz, 2H), 2.32 (m, 1H), 2.10-1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 145.6, 131.8, 128.6, 126.8, 126.4, 124.1, 39.0, 34.0, 33.3, 30.8. IR (cm^{-1}) = 3027, 2920, 2839, 978, 755, 698. GC-MS: Rt = 17.37 min; M^+ = 192.1 calculated for $C_{12}H_{13}Cl$, experimental = 192.1.

2-phenyl-1-chloro-cyclohexene (6d).[18] Ketone **5d** (261 mg, 1.50 mmol) was dissolved in CH_2Cl_2 (7.5 mL) along with triphosgene (445 mg, 1.50 mmol) and pyridine (485 µL, 6.00 mmol). After aqueous workup, the crude mixture was purified with column chromatography on silica gel, buffered with 1% Et_3N, using 100% hexanes to afford vinyl chloride **6d** (121 mg, 0.63 mmol) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.40-7.36 (m, 2H), 7.31-7.28 (m, 3H), 2.53-2.50 (m, 2H), 2.44-2.39 (m, 2H), 1.87-1.77 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 141.6, 134.4, 128.1, 128.1, 127.8, 126.9, 34.1, 33.0, 23.9, 22.7. IR (cm^{-1}) = 3055, 3022, 2932, 2860, 1003, 756, 698. GC-MS: Rt = 16.90 min; M^+ = 192.1 calculated for $C_{12}H_{13}Cl$, experimental = 192.1. The minor regioisomer was not isolable presumably due to its instability to column chromatography.

2-*sec*-butyl-1-chloro-cyclohexene (6e). Ketone **5e** (338 µL, 2.00 mmol) was dissolved in CH_2Cl_2 (10.0 mL) along with triphosgene (593 mg, 2.00 mmol) and pyridine (647 µL, 8.00

mmol). After aqueous workup, the crude mixture was purified with column chromatography on silica gel, buffered with 1% Et_3N, using 100% hexanes to afford vinyl chloride **6e** (118 mg, 0.68 mmol) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 2.58-2.49 (h, *J* = 7.2 Hz, 1H), 2.30-2.16 (m, 2H), 2.07-1.90 (m, 2H), 1.75-1.69 (m, 2H), 1,63-1.57 (m, 2H), 1.31 (p, *J* = 7.4 Hz, 2H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.81 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 148.7, 144.1, 129.7, 34.4, 27.1, 26.4, 22.8, 22.4, 22.1, 18.2, 12.2. IR (cm^{-1}) = 2962, 2934, 2874, 1782, 1129, 1061, 847. GC-MS: Rt = 12.61 min; M^+ = 172.1 calculated for $C_{10}H_{17}Cl$, experimental = 172.1. HR-MS: $(M\text{-}H\text{+}O)^{\bullet+}$ = 187.0885 calculated for $C_{10}H_{16}ClO$, experimental = 187.0880. The minor regioisomer was not isolable presumably due to its instability to column chromatography.

1,1'-[(1E/Z)-2-chloro-1-propene-1,3-diyl]bis-benzene (6f).[19] Ketone **6f** (210 mg, 2.00 mmol) was dissolved in CH_2Cl_2 (4.0 mL) along with triphosgene (593 mg, 2.00 mmol) and pyridine (647 µL, 8.00 mmol). Without aqueous workup, the crude mixture was directly purified with column chromatography on neutral alumina using 100% pentane to afford vinyl chloride **6f** (104 mg, 0.46 mmol) as colorless oil in a mixture of 5:1 *Z*:*E* olefin isomers. ^{1}H NMR (400 MHz, $CDCl_3$, *denoted the minor isomer); δ (ppm) = 7.64 (d, *J* = 7.4 Hz, 2H), 7.41-7.28 (m, 10H), 6.99 (s, 0.2H)*, 6.57 (s, 1H), 3.96 (s, 0.4H)*, 3.83 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, *denoted the minor isomer); δ (ppm) = 137.4, 135.0, 133.5, 130.1*, 129.1, 129.1, 128.7*, 128.6, 128.5*, 128.2, 127.7, 127.6*, 127.0, 126.8*, 125.9, 47.4, 40.6*. IR (cm^{-1}) = 2916, 2849, 2067, 2046, 1493, 1453, 750, 695. GC-MS for major isomer: Rt = 20.02 min; M^+ = 228.7 calculated for $C_{15}H_{13}Cl$, experimental = 228.1. GC-MS for minor isomer: Rt = 20.43 min; M^+ = 228.7 calculated for $C_{15}H_{13}Cl$, experimental = 228.1. Major olefin isomer was determined by NOESY experiment (see supporting information).

1-chloro-vinylbenzene (6g).[11b] Ketone **5g** (233 μL, 2.00 mmol) was dissolved in CH_2Cl_2 (4.0 mL) along with triphosgene (593 mg, 2.00 mmol) and pyridine (647 μL, 8.00 mmol). Without aqueous workup, the crude mixture was directly purified with column chromatography on silica gel, buffered with 1% Et_3N, using 100:0 → 98:2 → 96:4 hexanes : EtOAc to afford vinyl chloride **6g** (90 mg, 0.65 mmol) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.66 (dd, *J* = 2.1 and 7.7 Hz, 2H), 7.40-7.38 (m, 3H), 5.80 (d, *J* = 1.9 Hz, 1H), 5.56 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 140.0, 136.9, 129.1, 128.3, 126.4, 112.7. IR (cm^{-1}) = 2925, 1774, 1446, 1220, 879, 768, 670. GC-MS: Rt = 10.66 min; M^+ = 138.0 calculated for C_8H_7Cl, experimental = 138.1.

1-(1-chloroethenyl)-4-methoxy-benzene (6h).[20] Ketone **5h** (300 mg, 2.00 mmol) was dissolved in CH_2Cl_2 (4.0 mL) along with triphosgene (593 mg, 2.00 mmol) and pyridine (647 μL, 8.00 mmol). Without aqueous workup, the crude mixture was directly purified with column chromatography on neutral alumina using 100:0 → 98:2 → 92:8 pentane : EtOAc to afford vinyl chloride **6h** (74 mg, 0.44 mmol) as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.57 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.65 (d, *J* = 1.8 Hz, 1H), 5.41 (d, *J* = 1.8 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 160.3, 139.6, 129.6, 127.8, 113.6, 110.8, 55.4. IR (cm^{-1}) = 2916, 2849, 2068, 2045, 1605, 1487, 1254, 834, 676. GC-MS: Rt = 14.62 min; M^+ = 168.0 calculated for C_9H_9ClO, experimental = 168.0.

1-(1-chloroethenyl)-4-nitro-benzene (6i). Ketone **5i** (330 mg, 2.00 mmol) was dissolved in CH_2Cl_2 (4.0 mL) along with triphosgene (593 mg, 2.00 mmol) and pyridine (647 μL, 8.00 mmol). After aqueous workup, the crude mixture was purified with column chromatography on silica gel, buffered with 1% Et_3N, using 100:0 → 95:5 → 85:5 hexanes : EtOAc to afford vinyl chloride **6i** (198 mg, 1.08 mmol) as yellow crystals in a 5:1 mixture with *geminal*-dichloride product **7**. ^{1}H NMR (400 MHz, $CDCl_3$, *denoted the minor product); δ (ppm) = 8.24 (d, *J* = 8.9 Hz)*, 8.21 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.9 Hz)*, 7.78 (d, *J* = 8.8 Hz, 2H), 5.94 (d, *J* = 2.1 Hz, 1H), 5.73 (d, *J* = 2.1 Hz, 1H), 2.56 (s, 3H)*. ^{13}C NMR (100 MHz, $CDCl_3$, *denoted the minor product); δ (ppm) = 147.9,* 142.7, 137.8,* 127.2, 126.8,* 123.6, 123.6,* 116.5, 38.6.* IR (cm^{-1}) = 2916, 2849, 2066, 2046, 1523, 1344, 859, 700. GC-MS of the major product: Rt = 16.56 min; M^+ = 183.0 calculated for $C_8H_6ClNO_2$, experimental = 183.0. GC-MS for the minor product: Rt = 17.83 min; M^+ = 219.0 calculated for $C_8H_7Cl_2NO_2$, experimental = 219.0. HR-MS: $(M+H)^+$ 184.0163 calculated for $C_8H_7ClNO_2$, experimental 184.0160.

1-chloro-3,4-dihydronaphtalene (6j).[11b] Ketone **5j** (266 μL, 2.00 mmol) was dissolved in CH_2Cl_2 (4.0 mL) along with triphosgene (593 mg, 2.00 mmol) and pyridine (647 μL, 8.00 mmol). After aqueous workup, the crude mixture was purified with column chromatography on silica gel using 100% hexanes to afford vinyl chloride **6j** (177 mg, 1.08 mmol) as orange oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.72 (1H, d, *J* = 7.5 Hz), 7.39-7.31 (2H, m), 7.24 (1H, d, *J* = 7.4 Hz), 6.29 (1H, t, *J* = 4.6 Hz), 2.94 (2H, t, *J* = 8.0 Hz), 2.52-2,47 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 136.4, 132.5, 130.6, 128.3, 127.4, 126.8, 126.1, 124.2, 27.7, 24.3. IR (cm^{-1}) = 2934, 2888, 2833, 1161, 812, 758. GC-MS: Rt = 15.28 min; M^+ = 164.0 calculated for $C_{10}H_9Cl$, experimental = 164.1.

1,3-dichloro-1,3-cyclohexadiene (6k).[21] Diketone **5k** (224 mg, 2.00 mmol) was dissolved in CH_2Cl_2 (10.0 mL) along with triphosgene (593 mg, 2.00 mmol) and pyridine (647 μL, 8.00 mmol). Without aqueous workup, the crude mixture was directly purified with column chromatography on silica gel, buffered with 1% Et_3N, using 100% hexanes to afford bis(vinyl chloride) **6k** (120 mg, 0.81 mmol) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 5.99

(q, J = 1.6 Hz, 1H), 5.75 (td, J = 4.5 and 1.6 Hz, 1H), 2.56-2.50 (m, 2H), 2.47-2.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 134.7, 126.7, 123.9, 119.7, 29.9, 24.4. IR (cm^{-1}) = 2949, 2886, 2832, 1632, 1591, 1351, 1059, 805, 766, 731. GC-MS: Rt = 10.31 min; M^+ = 148.0 calculated for $C_6H_6Cl_2$, experimental = 148.0.

3-chloro-1-phenylbutadiene (6l).[11b] Ketone **5l** (292 mg, 2.00 mmol) was dissolved in CH_2Cl_2 (4.0 mL) along with triphosgene (593 mg, 2.00 mmol) and pyridine (647 μL, 8.00 mmol). After aqueous workup, the crude mixture was purified with column chromatography on silica gel using 100% hexanes to afford divinyl chloride **6l** (81 mg, 0.49 mmol) as orange oil, which appeared to rapidly decompose upon isolation. GC-MS: Rt = 14.87 min; M^+ = 164.0 calculated for $C_{10}H_9Cl$, experimental = 164.1.

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SUPPORTING INFORMATION

GC-MS chromatograms for Figure 1 and Table 1, as well as ^{1}H and ^{13}C NMR spectra for characterized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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