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Reaction of trihaloisocyanuric acids with alkynes: an efficient methodology for the preparation of β-haloenol acetates

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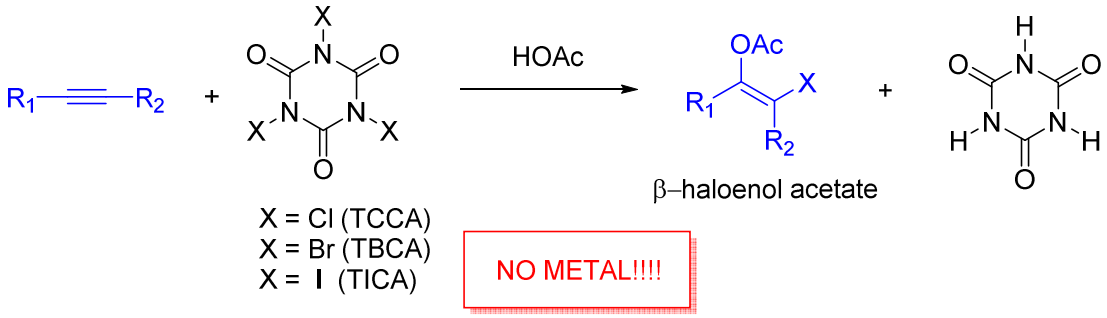
Abstract

The reaction between trihaloisocyanuric acids and alkynes in the presence of acetic acid provides an efficient methodology for preparation of β-haloenol acetates in yields ranging from 34 to 94%, depending on the halogen and alkynes used. This methodology provides an alternative to typical procedures, which usually employ metal catalysis and are limited to terminal alkynes.



Keywords: Trihaloisocyanuric acids, β-haloenol acetates, electrophilic halogenation, alkynes

Introduction

Trihaloisocyanuric acids (TXCA, Fig. 1) are inexpensive cyclic ureas used as versatile and green electrophilic halogenating agents.[1-5] Among the haloisocyanuric acids, the most employed is the trichloroisocyanuric, or TCCA (X = Cl), a stable solid used for swimming pool disinfection, sold in supermarkets or specialized stores on multigram/kilogram scale.[6] Tribromoisocyanuric acid (TBCA, X = Br), although not yet widely commercially available, can be easily obtained from cyanuric acid, KBr and oxone, in a safe procedure.[7] Triiodoisocyanuric acid (TICA, X = I) can be obtained from TCCA and I_2, heated in a sealed tube at high temperatures.[8] Mixed trihaloisocyanuric acids are also known.[9,10] All these reagents have been shown to be very efficient halenium (X^+) releasing agents in diverse reactions, affording good to excellent yields of the desired halogenated products. Therefore, depending on the nature of the nucleophile reacting with these electrophilic agents, different products can be obtained, such as haloarenes, halohydrins, halocarbonyls, etc.[1,5,6] The trihaloisocyanuric acids also are very interesting reagents from the Green Chemistry point of view, since they present good atom economy and are safe to be handled. After the reaction is completed, its by-product, the isocyanuric acid can be easily separated from the reaction media by simple filtration and can be reused for the synthesis of new TXCA batches.[11]

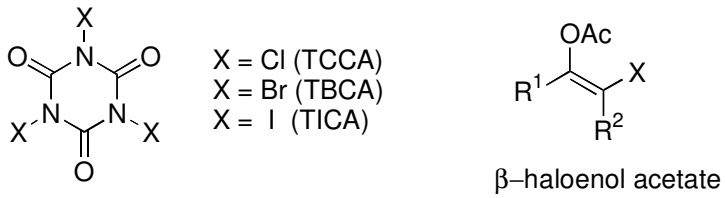
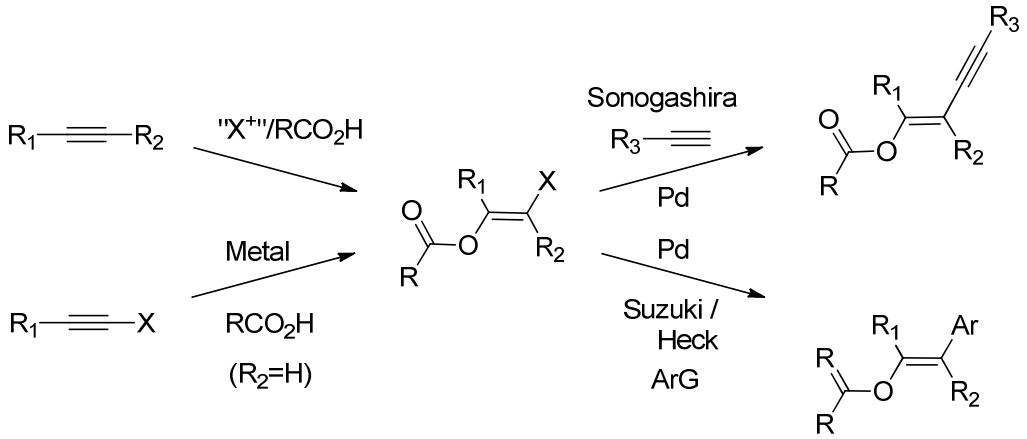


Figure 1. Structures of the trihaloisocyanuric acids and β-haloenol acetates.

β-Haloenol acetates (Figure 1) are key intermediates for diverse chemical transformations (Scheme 1), since they hold both enol acetate moiety as well as carbon-halogen reactivities, which can be explored in numerous synthetic ways.[12] They can be prepared from an electrophilic halogen attack to alkynes, as demonstrated for instance by Barluenga *et al.*,[13] or by metallic catalysis using haloalkynes.[12,14,15] Nevertheless, those methodologies usually need terminal haloalkynes and fancy metal catalysis, or are generally limited to iodo derivatives which shrink their synthetic scope.

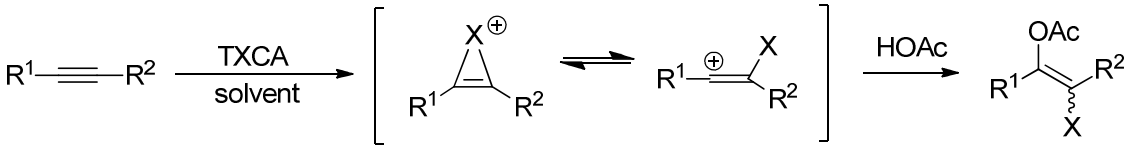


Scheme 1

Continuing our interest on the chemistry of trihaloisocyanuric acids, we have considered the use of TXCA as electrophilic reagent in the reaction with alkynes in order to prepare the interesting β-haloenol acetates, which are synthetically appealing building blocks. Herein we report the results of our researches.

Results and Discussion

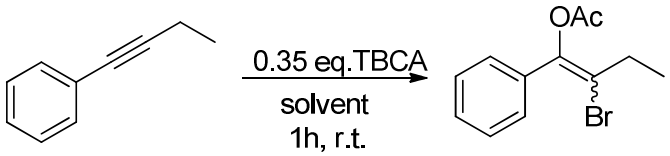
In order to obtain the desired β-haloenol acetates, we have reacted selected alkynes with TXCA in the presence of acetic acid, according to the strategy shown in Scheme 2.



Scheme 2

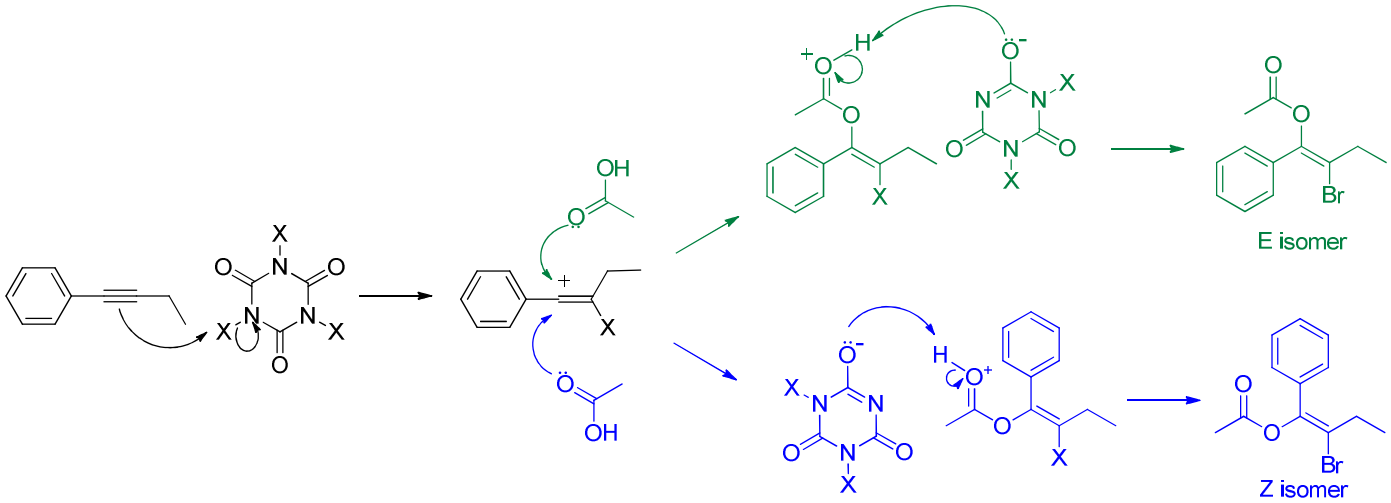
Initially the reaction was carried out with TBCA and 1-phenyl-1-butyne (1 mol equiv.), in the presence of HOAc at room temperature, in order to optimize the reaction conditions, being the results shown in Table 1. The use of HOAc as solvent (Table 1, entry 1) afforded the expected β-bromoenol acetate along with minor amount (3%) of the corresponding β-dibromoketone, due to the hydrolysis of the products. In order to avoid this by-product we replaced HOAc by acetic anhydride (Ac_2O), which afforded the desired product although in low conversion (Table 1, entry 2). Addition of 1 eq. of HOAc improved the yields, but still conversion was low (Table 1, entry 3). The use of 1:1 (v/v) mixture of Ac_2O and HOAc finally afforded only the β-bromoenol acetate in quantitative conversion after 1h (Table 1, entry 4) and 87% isolated yield. According to GC-MS and NMR analysis a mixture of *Z* and *E* diastereoisomers is formed under these conditions. Solvents with different polarities were used in order to evaluate the change in the ratio of these stereoisomers. The results show that in all cases approximately the same proportion of the *E* and *Z* stereoisomers is obtained regardless the solvent employed, only the conversion being affected by the solvent change. This suggests that the conjugated vinyl cation is being formed as intermediate instead of the corresponding bromonium ion (Scheme 3).

Table 1. Solvent influence on the reaction between TBCA and 1-phenyl-1-butyne



Entry	Solvent	Conversion (%)[a]	*E*:*Z* ratio
1	AcOH	97[b]	88:12
2	Ac_2O	24[c]	88:12
3	Ac_2O/1eq. AcOH	76	88:12
4	Ac_2O:AcOH (1:1)	100[d]	85:15
5	CH_2Cl_2	34	87:13
6	Hexane	22[e]	86:14

[a] Determined by GC-MS; [b] 3% of the corresponding dibromoketone formed; [c] incomplete reaction; [d] 87% isolated yield; [e] 65% after 4 days.



Scheme 3

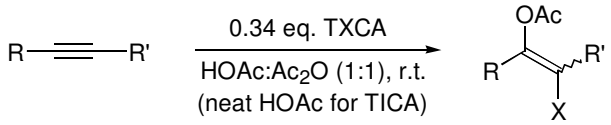
Based upon this initial study we chose the 1:1 mixture of HOAc:Ac_2O as standard conditions for the reaction of TXCA with other alkynes (2 mmol of substrate, and 0.68 mmol of TBCA in 6 mL of solvent at room temperature). The reaction was monitored by GC-MS until complete conversion of the substrate and in all cases the expected β-haloenol acetates were obtained, as shown in Table 2.

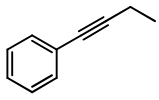
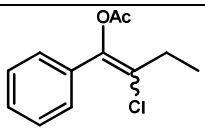
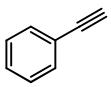
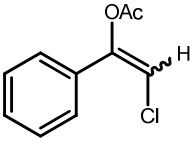
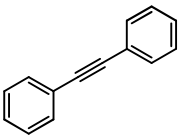
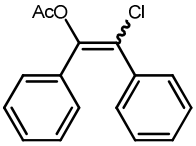
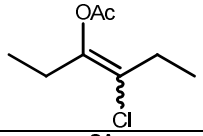
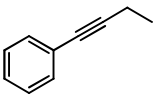
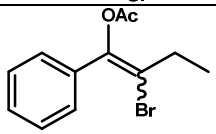
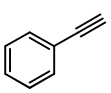
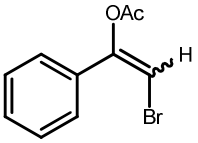
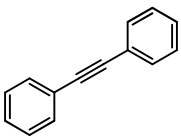
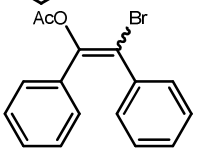
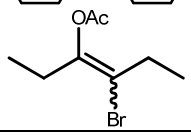
The reactions of alkynes with TBCA in HOAc/Ac_2O to produce the corresponding β-bromoenol acetates in high regiolectivity are depicted in Table 2 entries 5-8. The reactions gave good to excellent yield with exception of phenylacetylene that formed, in addition to the desired β-haloenol acetate, the corresponding α,α-dibromocarbonyl product (formed from the hydrolyzed product) as well as the ring-brominated products (Scheme 4). Attempts to improve the formation of the β-bromoenol acetate by lowering the reaction temperature to 15°C resulted in no change in the reaction outcome. GC-MS monitoring of the reaction confirms that those by-products are formed from its inception, which demands further product column purification. After purification, the mixture of the stereoisomers, which we could not separate, was obtained in 51% yield (Table 2, entry 6). On the other hand the β-bromoenol acetate derived from 3-hexyne, was obtained as a single stereoisomer, indicating the corresponding bromonium ion as reaction intermediate. Attempts of purifying this compound by column chromatography resulted in degradation (Table 2, entry 8).

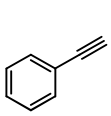
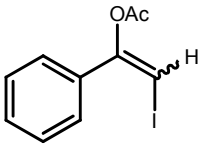
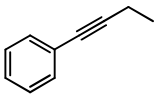
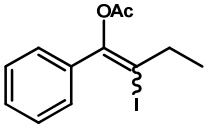
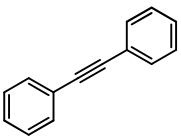
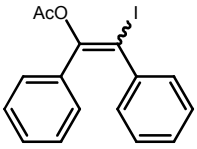
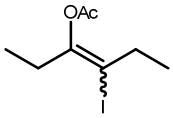
Similar results were obtained by reacting the alkynes with TCCA (Table 2, entries 1-4). Once more, using phenylacetylene as substrate, α,α-dichloroacetophenone and ring chlorination products were also observed (Scheme 4). The reaction with 1-phenyl-1-butyne was purified by flash chromatography, also affording the mixture of stereoisomers. The reaction of diphenylacetylene only resulted in the mixture of diasteroisomers, with no need of further purification (Table 2, entry 3). Attempts of purifying the product from 3-hexyne (Table 2, entry 4) by flash chromatography failed, since it degrades on column.

Finally, the reaction of alkynes with TICA also led to the corresponding β-iodoenol acetates, but the reactions are much slower as shown by the reaction times in Table 2, entries 9-12. This led us to carry out most of the reaction in neat HOAc. Therefore, 1-phenyl-2-iodovinylacetate was efficiently obtained after 4h of reaction as demonstrated by NMR analysis. However, upon isolation, a rapid color change of the product to violet was observed. Purification attempts of this product by column chromatography were unsuccessful, since degradation takes place. Reaction of TICA with phenylacetylene is cleaner, resulting on the corresponding β-iodoenol acetate after 3h of reaction. The reaction product was found to be more stable, since it presented

Table 2. Monohalogenation of different alkynes with TXCA

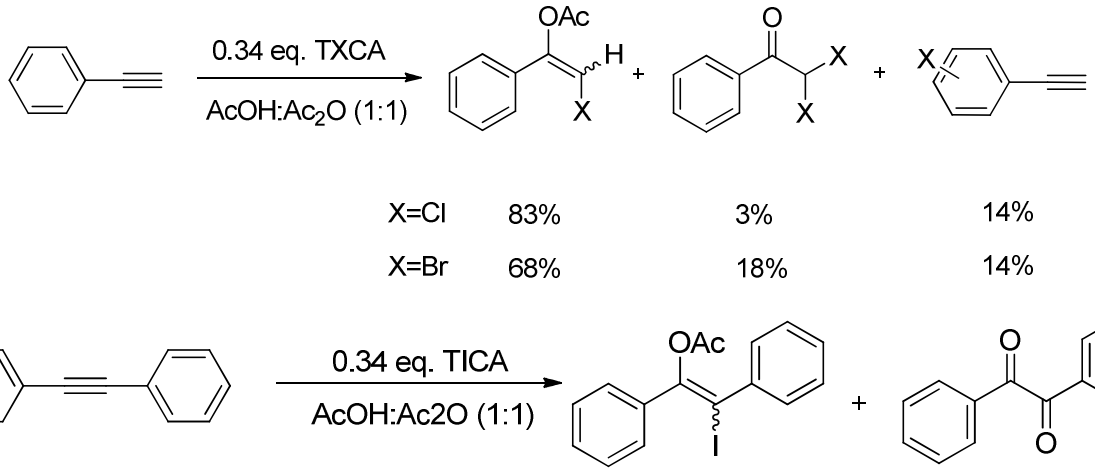


Entry	Substrate	Product	Time (h)	Yield (%)[a]	*E:Z*[b]
1			1	57	51:49
2			6	49	63:37
3			6.5	98	33:67
4			1	78[c]	n.d.
5			1	87	85:15
6			3	51	69:31
7			6.3	89	77:23
8			1	62[c]	100:0

9			4	40[c]	n.d.
10			3	86	100:0
11[b]			16	34	87:13
12			2.5	79[d]	n.d.

[a] Isolated yield; [b] Determined by GC-MS; [c] crude; [d] reaction at 0 [o]C.

satisfactory purity after reaction workup (Table 2, entry 9). The synthesis of the 1,2-diphenyl-2-iodoenol acetate from diphenylacetylene was initially carried out under the same conditions as the previous iodination reactions, but under these condition and 14 days, there still was starting material left as well as considerable quantities of benzil. To prevent formation of this product, the reaction was carried out using the 1:1 HOAc:Ac_2O mixture at 0 ^oC, leading to a decrease of the amounts of benzil from 29% to 4%. After flash chromatography, 34% yield of the mixture of stereoisomers was obtained (Table 2, entry 10). Once again the reaction of TICA with 3-hexyne affording the 4-iodo-3-acetoxy-3-hexene was obtained in 79% yield (crude) and 84% purity (table 2, entry 12). Its purification by flash chromatography was not possible, since it degradates on column.



Scheme 4

Conclusions

We have shown that β-haloenol acetates can be efficiently obtained by reacting alkynes with trihaloisocyanuric acids in HOAc, Ac_2O or a mixture of these solvents. A mixture of *Z* and *E* stereoisomers of

the corresponding β-haloenol acetate is generally obtained for conjugated alkynes, indicating the intermediacy of resonance stabilized vinyl cations, instead of the corresponding halonium ions in this case.

Experimental Section

General. TCCA and the alkynes were purchased from Sigma-Aldrich and used as received, while TBCA and TICA were synthesized according to the procedure previously reported by us.[7,8] Solvents were purchased from Tedia and Vetec, and used without purification, unless otherwise stated.

NMR spectra were recorded on a Bruker spectrometer models AC-200 or AC-300. The spectra of NOESY-1D, NOESY-2D, COSY, HETCOR (in Supporting Information), as well as some ^{1}H and ^{13}C NMR analyses were obtained in a Varian 600-NMR. HRGC-MS analyses were performed on a Shimadzu GCMS-QP2010S gas chromatograph with electron impact (70 eV) by using a 30 m DB-5 silica capillary column. Diastereoisomeric ratios were determined by GC-MS, and the major component was determined by NMR.

Flash chromatography was carried out for purifying the products using a 15-20 mm diameter column, with 25 cm of silica gel (230-400 mesh) and 5% ethyl acetate:hexane mixture as eluent.

General procedure. In a 10 mL round bottom flask, 0.34 mmol of TXCA was added to a stirred mixture of 6 mL of solvent and the substrate (HOAc for iodinations and 1:1 (v/v) mixture of HOAc:Ac_2O for the chlorination and brominations). GC-MS analyses were carried out to evaluate the extension of the reaction and, after its completion; 10 mL of distilled water were added to the reaction medium, followed by addition of of 10% $NaHSO_3$ (10 mL). The aqueous phase was then extracted with ethyl acetate (1 x 20 mL + 2 x 10 mL) and the combined organic phase was washed with a saturated aqueous solution of $NaHCO_3$, dried (Na_2SO_4), filtered and evaporated under vacuum (rotatory evaporator). The crude products were obtained by flash chromatography. NMR and MS analyses were carried out.

2-Bromo-1-phenylbut-1-en-1-yl acetate.[16] $C_{12}H_{13}BrO_2$; MM 269; pale yellow oil. Yield: 87% (468.1 mg; mixture of diastereoisomers *E*:*Z* = 88:12). IR (KBr) ν /cm^{-1}: 3057, 2976, 2938, 1765, 1981, 1200, 1088, 1057, 1021, 699 ^{1}H NMR (300 MHz, $CDCl_3$): δ diastereoisomer *E*) = 1.22-1.29 (t, *J*= 8.0Hz, 3H, CH_3); 2.14 (s, 3H, $COCH_3$); 2.58-2.69 (q, *J*= 8.0Hz, 2H, CH_2); 7.36-7.44 (m, H3, 3Ar-H); 7.59-7.64 (m, H2, 2Ar-H). δ diastereoisomer *Z*) = 1.29-1.39 (t, *J*= 8Hz, 3H, CH_3); 2.19 (s, 3H, $COCH_3$); 2.69-2.83 (q, J= 8.0Hz, 2H, CH_2); 7.36-7.44 (m, H3, 3Ar-H); 7.59-7.64 (m, H2, 2Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ diastereoisomer *E*)= 12.9 (CH_3); 20.8 (CH_3); 29.0 (CH_2); 120.9 (C); 128.0 ($_{m\text{-}}CH$); 128.9 ($_{p\text{-}}CH$); 129.4 ($_{o\text{-}}CH$); 135.5(C_{Ar}); 143.3 (C); 168.5 (CO). δ diastereoisomer *E*)= 13.8 (CH_3); 20.8 (CH_3); 29.5 (CH_2); 121.5 (C); 128.6 ($_{m\text{-}}CH$); 128.7 ($_{o\text{-}}CH$); 129.2 ($_{p\text{-}}CH$); 134.2(C_{Ar}); 144.3 (C); 168.1 (CO). MS *m/z* (%): 226 (59%) and 228 (53%), 211 (48%) and 213 (46%), 189 (100%), 147 (25%) 132 (33%), 105 (28%), 77 (67%), 43 (68%).

2-Bromo-1-phenylvinyl acetate.[17] $C_{10}H_9BrO_2$; MM 241; pale yellow oil. Yield: 51% (245.8 mg; mixture of diastereoisomers *E:Z* = 69:31). IR (KBr) ν /cm^{-1}: 3092, 1760, 1250, 1164, 1056, 697. ^{1}H NMR (600 MHz, $CDCl_3$): δ diastereoisomer *E*) = 2.19 (s, 3H, CH_3); 6.35 (s, 1H, CH); 7.37-7.43 (m, H_{Ar}); 7.66-7.67 (m, H_o). δ diastereoisomer *Z*) =2.36 (s, 3H, CH_3); 6.58 (s, 1H, CH); 7.37-7.43 (m, H_{Ar}); 7.66-7.67 (m, H_o). ^{13}C NMR (150 MHz, $CDCl_3$): δ diastereoisomer *E*) = 20.9 (CH_3); 97.8 (CH); 128.3 (CH_o); 128.4 (CH_m); 129.6 (CH_p); 133.4 (C_{Ar}); 148.9 (C); 168.8 (CO). δ diastereoisomer *Z*) = 20.7 (CH_3); 96.7 (CH); 125.0 (CH_o); 128.9 (CH_m); 134.1 (C_{Ar}); 150.6 (C); 167.4 (CO). MS *m/z* (%): 198 (77%) and 200 (72%), 161 (56%), 120 (17%) and 122 (16%), 78 (68%), 77 (23%), 51 (21%), 43 (100).

2-Bromo-1,2-diphenylvinyl acetate.[18] $C_{16}H_{13}BrO_2$; MM 317; pale yellow solid. Yield: 89% (564.3 mg; mixture of diastereoisomers *E*:*Z* = 72:28). IR (KBr) ν /cm^{-1}: 3099, 3081, 3055, 3034, 1762, 1640, 1444, 1194, 1178, 1061, 1023, 756, 700. ^{1}H NMR (200 MHz, $CDCl_3$): δ diastereoisomer *E*) = 2.00 (s, 3H, CH_3); 7.31-7.81 (m, H_{Ar}). δ diastereoisomer *Z*) = 2.39 (s, 3H, CH_3); 7.31-7.81 (m, H_{Ar}) ^{13}C NMR (50 MHz, $CDCl_3$): δ diastereoisomer *E*) = 20.7 (CH_3); 114.2 (C); 128.2 (CH_m); 128.4 (CH_m); 128.8 (CH_p); 128.9 (CH_o); 129.3 (CH_o); 135.5 (C_{Ar}); 146.1 (C); 168.7 (CO). δ diastereoisomer *Z*) =21.0 (CH_3); 115.2 (C); 128.2 (CH_m); 128.4 (CH_m); 128.8 (CH_p); 129.3 (CH_o); 130.4 (CH_o); 134.1 (C_{Ar}); 144.7 (C); 168.0 (CO). MS *m/z* (%): 316 (M^+; 0.1%) and 318 ($(M+2)^+$; 0.1%), 274 (84%) and 276 (81%), 237 (78%), 194 (23%), 165 (66%), 105 (43%), 77 (54%), 51 (18%), 43 (110%).

4-Bromohex-3-en-3-yl acetate. $C_8H_{13}BrO_2$; MM 221; pale yellow oil. Yield: 62% (274.0 mg; crude) ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.98-10.60 (t, *J* = 7.3Hz, 3H, CH_3); 1.02-1.09 (t, *J* = 7.5Hz, 3H, CH_3); 2.17 (s, 3H, CH_3); 2.29-2.40 (q, *J*=7.3, 2H, CH_2); 2.43-2.54 (q, *J*=7.5Hz, 2H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.8 (CH_3); 12.8 (CH_3); 20.7 (CH_3); 26.4 (CH_2); 28.1 (CH_2); 119.2 (C); 146.9 (C); 168.7 (CO). MS - *m/z* (%): 178 (40%) and 180 (38%), 163 (36%) and 165 (33%), 141 (24%), 99 (21%), 55 (26%), 43 (100%).

2-Chloro-1-phenylvinyl acetate.[19] $C_{10}H_9ClO_2$; MM 196 g/mol, pale yellow oil. Yield: 49% (192.0 mg; mixture of diastereoisomers *E:Z* = 63:37). IR (KBr) ν /cm^{-1}: 3515, 3086, 2932, 1770, 1493, 1446, 1370, 1202, 1180, 1064, 1029, 754, 697. ^{1}H NMR (600 MHz, $CDCl_3$): δ diastereoisomer *E*) = 2.21 (s, 3H, CH_3); 6.27 (s, 1H, CH); 7.37-7.43 (m, H_{Ar}); 7.65-7.66 (m, H_o). δ diastereoisomer *Z*) =2.35 (s, 3H, CH_3); 6.47 (s, 1H, CH); 7.37-7.43 (m, H_{Ar}); 7.65-7.66 (m, H_o). ^{13}C NMR (150 MHz, $CDCl_3$): δ diastereoisomer *E*) = 21.0 (CH_3); 110.6 (CH); 128.1 (CH_o); 128.5 (CH_m); 129.6 (CH_p); 132.4 (C_{Ar}); 148.0 (C); 169.1 (CO). δ diastereoisomer *Z*) = 20.7 (CH_3); 108.2 (CH); 124.9 (CH_o); 129.0 (CH_m); 129.6 (CH_p); 133.0 (C_{Ar}); 148.7 (C); 167.6 (CO). MS - *m/z* (%): 196 (M^+; 2.5%) and 198 ($(M+2)^+$; 0.8%), 154 (52%) and 156 (17%), 105 (5%), 78 (66%), 77 (20%), 51 (17%), 43 (100%).

2-Chloro-1-phenylbut-1-en-1-yl acetate.[16,20] $C_{12}H_{13}ClO_2$; MM 224, pale yellow oil. Yield: 57% (255.4 mg; mixture of diastereoisomers *E:Z* = 51:49) ^{1}H NMR (200 MHz, $CDCl_3$): δ diastereoisomer *E*) = 1.18 (t, *J*= 8.0Hz, 3H, CH_3); 2.15 (s, 3H, CH_3); 2.17-2.51 (q, *J*= 8.0Hz, 2H, CH_2); 7.31-7.39 (m, 5Ar-H). δ diastereoisomer *Z*) = 1.25 (t, *J*= 8Hz, 3H, CH_3); 2.17 (s, 3H, CH_3); 2.15-2.49 (q, *J*= 8.0Hz, 2H, CH_2); 7.31-7.39 (m, 5Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ diastereoisomers *E* and *Z*)= 12.8 and 11.9 (CH_3); 20.7 and 20.8 (CH_3); 29.9 and 27.8 (CH_2), 128.1 and 128.6 (CH_m); 128.8 and 128.9 (CH_o); 129.1 (CH_p); 134.3 and 134.1 (C); 168.2 and 168.7 (CO). MS *m/z* (%): 224 (M^+; 1.5%) and 226 $(M+2)^+$; 0.5%), 189 (19%), 182 (65%) and 184 (21%), 167 (54%) and 169 (18%), 147 (16%), 131 (23%), 105 (23%), 89 (23%), 77 (63%), 51 (25%), 43 (100%).

2-Chloro-1,2-diphenylvinyl acetate.[18,20] $C_{16}H_{13}ClO_2$; MM 272, pale yellow solid. Yield: 98% (533.1 mg; mixture of diastereoisomers *E:Z*=33:67) ^{1}H NMR (200 MHz, $CDCl_3$): δ diastereoisomer *Z*) = 2.31 (s, 3H, CH_3); 7.21-7.73 (m, 10H, H_{Ar}). δ diastereoisomer *E*) = 1.98 (s, 3H, CH_3); 7.21-7.73 (m, 10H, H_{Ar}). ^{13}C NMR (50 MHz, $CDCl_3$): δ (diastereoisomer *Z*) = 20.9 ($1CH_3$); 124.2 (1C); 128.3 ($2CH_m$); 128.5 ($2CH_m$); 129.0 ($2CH_o$); 129.3 ($2CH_o$); 130.1 ($2CH_p$); 134.4 ($1C_{Ar}$); 136.2 ($1C_{Ar}$); 144.4 (1C); 168.1 (1CO). δ (diastereoisomer *E*) = 20.9 ($1CH_3$); 124.0 (1C);128.3 ($2CH_m$); 128.5 ($2CH_m$); 129.0 ($4CH_o$); 130.1 ($2CH_p$); 128.8 ($2CH_p$); 134.1 ($1C_{Ar}$); 136.5 ($1C_{Ar}$);143.6 (1C); 168.9 (1CO). MS *m/z* (%): 272 (M^+; 3.3%) and 274 $(M+2)^+$; 1.2%), 230 (100%) and 232 (32%), 195 (10%), 165 (40%), 152 (30%), 124 (32%), 105 (28%), 89 (20%), 77 (50%), 51 (15%), 43 (74%).

4-Chlorohex-3-en-3-yl acetate: $C_8H_{13}ClO_2$; MM 176, pale yellow oil. Yield: 78% (274.6mg; crude). MS - *m/z* (%): 176 and 178 (M+ and (M+2)+/0.4 and 0.14%), 141 (20%), 134 and 136 (53 and 17.5%), 119 and 121 (64 and 21.5%), 99 (23%), 55 (26%), 43 (100%).

2-Iodo-1-phenylvinyl acetate.[19,21] $C_{10}H_9IO_2$; MM: 288, pale yellow oil, degrade. Yield: 40%. MS - *m/z* (%): 288 (1%), 246 (100%), 168 (29%), 161 (27%), 105 (17%), 91 (19%), 77 (15%), 51 (16%), 43 (66%).

(*E*)-2-Iodo-1-phenylbut-1-en-1-yl acetate. $C_{12}H_{13}IO_2$; MM 316, pale yellow oil. Yield: 86% (543.5 mg). IR (KBr) ν /cm^{-1}: 3056, 2972, 1762, 1350, 1198, 1082, 1050, 1018, 699. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.14-1.17 (t, *J*= Hz,

3H, CH_3); 2.13 (s, 3H, CH_3); 2.57-2.61 (q, *J*= Hz, 2H, CH_2); 7.34-7.51(m, 5H, H_{Ar}). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.2 (CH_3); 20.7 (CH_3); 32.2 (CH_2); 98.5 (C); 128.1 (CH_m); 129.1 (CH_p); 129.9 (CH_o); 137.6 (C_{Ar}); 145.9 (C); 168.5 (CO). MS *m/z* (%): 274(97%), 259 (58%), 189 (100%), 147 (23%), 132 (60%), 115 (26%), 105 (45%), 77 (94%), 69 (72%), 51 (36%), 43 (100%).

2-Iodo-1,2-diphenylvinyl acetate.[19,21] $C_{16}H_{13}IO_2$; MM 364, pale yellow oil. Yield: 34% (247.5 mg; mixture of diastereoisomers *E:Z* = 87:13). ^{1}H NMR (200 MHz, $CDCl_3$): δ diastereoisomer *E*) = 1.75 (s, 3H, CH_3); 7.06-7.92 (m, 10H, H_{Ar}). δ diastereoisomer *Z*) = 2.21 (s, 3H, CH_3); 7.06-7.92 (m, 10H, H_{Ar}). MS - *m/z* (%): 322 (90%), 237 (100%), 195 (87%), 177(33%), 165 (75%), 152 (21%), 105 (14%), 77 (25%), 51 (10%), 43 (62%).

4-Iodohex-3-en-3-yl acetate.[19,22] $C_8H_{13}IO_2$; MM 268, pale yellow oil. Yield: 79% (423.4 mg). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.98-1.04 (t, 6H, $2CH_3$); 2.17 (s, 3H, CH_3); 2.30-2.36 (q, 2H, CH_2); 2.51-2.58 (q, 2H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.0 (CH_3); 14.2 (CH_3); 20.6 (CH_3); 30.0 (CH_2); 31.4 (CH_2); 96.3 (C); 148.9 (C); 168.5 (CO). MS - *m/z* (%): 268 (M^+, 3%), 226 (100%), 211 (50%), 141 (34%), 99 (20%), 55 (20%), 43 (95%).

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Supplementary Material

Spectral characterization of the products is available in the Supplementary File.

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