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Article

A Green Hunsdiecker Reaction of Cinnamic Acids

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Os ácidos tribromo- e tricloro-isocianúricos reagem com ácidos cinâmicos na presença de $NaOH/H_2O/Et_2O$ à temperatura ambiente para produzir regiosseletivamente (*E*)-2-halo-estirenos em 25-95% de rendimento. Estudo sobre o mecanismo da reação utilizando correlações Hammett e cálculos DFT (teoria do funcional da densidade) mostraram que esta reação tem como passo determinante a velocidade da adição eletrofílica de um átomo de cloro à ligação dupla.

Tribromo- and trichloroisocyanuric acids react with cinnamic acids in $NaOH/H_2O/Et_2O$ at room temperature to produce (*E*)-2-halostyrenes regioselectively in 25-95% yield. Mechanism studies using Hammett correlations and DFT (density functional theory) calculations have shown that this reaction has as rate determining step the electrophilic addition of chlorine atom to the double bond.

Keywords: styrene, cinnamic acid, Hunsdiecker reaction, trihaloisocyanuric acid, DFT

Introduction

The halodecarboxylation of carboxylic acids, also known as Hunsdiecker reaction,[1] is an important route to the preparation of halogenated compounds. Formerly studied in 1940, it is the reaction of a silver salt of carboxylic acids with molecular halogen through a radical or electrophilic process to give CO_2 and an aryl or styryl halide. More recently, different metal salts, such as Hg(II),[2] Pb(II)[3] and Mn(IV)[4] and sources of electrophilic halogens (*N*-halosuccinimides,[5] molecular halogens,[6,7] KX/oxone®[8] and $NaBrO_3/NaHSO_3$)[9] have been used to improve the Hunsdiecker reaction.

The trihaloisocyanuric acids (Figure 1) are stable compounds that can transfer up to three electrophilic halogen atoms to organic compounds. The trichloroisocyanuric acid (TCCA) is a cheap solid found in commercial products for swimming-pool desinfection.[10] The tribromoisocyanuric acid (TBCA) is easily prepared from cyanuric acid in a green and very convenient route by the reaction of cyanuric acid with KBr/oxone®.[11] These acids are useful reagents from the green chemistry point of view, as they are safe, stable and have an excellent atom economy (46% for TCCA and 66% for TBCA). Besides, the residue formed in their reactions (cyanuric acid) can be recycled to reform the original trihaloisocyanuric acid.[12]

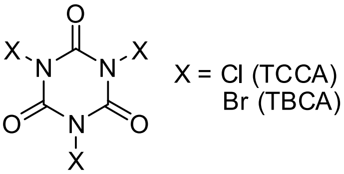

Figure 1. Structure of the trihaloisocyanuric acids.

Our goup has already shown that trihaloisocyanuric acids are efficient reagents to perform the cohalogenation[10,11] and halofluorination[13] of unsaturated compounds, preparation of epoxides,[14] and halogenation of aromatic[15] and dicarbonyl compounds.[16] In this work, it is communicated our results on a new green Hunsdiecker reaction of cinnamic acids using trichloro- and tribromoisocyanuric acids.

Results and Discussion

The bromodecarbonylation reaction of *p*-methoxycinnamic acid using tribromoisocyanuric acid in the traditional conditions used in Hunsdiecker reactions, i.e., NEt_3 as base and CH_2Cl_2 as solvent, led to (*E*)-2-bromo-*p*-methoxystyrene in 22% yield. In order to make the reaction more green, different conditions were evaluated (Table 1) to both avoid harmful chlorinated solvents and ease the workup process. The best results were obtained by stirring together the acid with TBCA (0.3 mol equiv.) in a biphasic system Et_2O/aqueous NaOH

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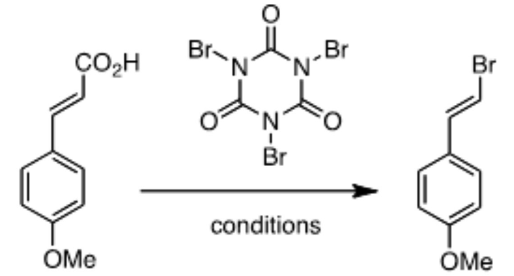
Table 1. Hunsdiecker reaction of *p*-methoxycinnamic acid



Condition	Yield[a] / %
NEt_3/CH_2Cl_2, room temperature, 15 min	22
Na_2CO_3/H_2O/hexane, room temperature, 20 min	60
$NaOH/H_2O/Et_2O$, room temperature, 20 min	55
H_2O/Et_2O, room temperature, 24 h	11

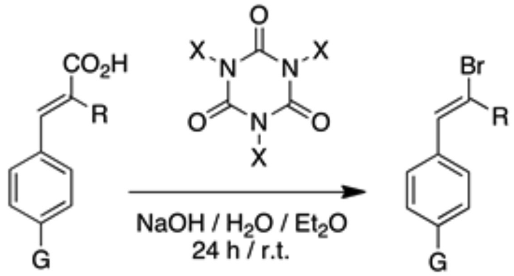
[a]Determined by HRGC using chlorobenzene as internal standard.

for 24 h at room temperature, leading to the corresponding 2-bromostyrene in 95% yield. Using these conditions, the workup process was very simple and convenient as the pure product (verified by ^1H and ^{13}C nuclear magnetic resonance (RNM) and high resolution gas chromatography (HRGC)) was easily obtained by separation of the ethereal layer from the reaction media followed by its evaporation. The reaction performed in the absence of base was incomplete after 24 h and led the bromostyrene in only 11% yield, along with unreacted *p*-methoxycinnamic acid and some unidentified minor products.

It is worth mentioning that reaction times were not optimized, which validates the possibility of either hexane or Et_2O to be used as extraction solvent without changes in the yield of the reaction. However, Et_2O was preferred to be used because it evaporates at softer conditions than hexane, avoiding the loss of product due to its high vapor pressure. Based on the above results, the Hunsdiecker reaction of several substituted cinnamic acids using the tribromo- and trichloroisocyanuric acids, NaOH as base and the biphasic media H_2O/Et_2O was also evaluated and the results are shown in Table 2. The yields of the 2-halostyrenes were highly dependent on the substituent of the aromatic ring. In general, reactions with TBCA gave higher yields and under these conditions, *p*-hydroxycinnamic acid led to several unidentified products, whilst both *o*- and *p*-nitrocinnamic acids were not reactive.

The products (2-halostyrenes) were analyzed by usual techniques (^1H and ^{13}C NMR and mass spectrometry (MS)). The reactions were highly stereoselective, with detection of a single product with *trans* stereochemistry, as determined by ^1H NMR from the coupling constant (*J*) of vinylic hydrogens (Figure 2). Exception was observed with α-methylcinnamic acid that afforded a mixture of geometric isomers, with predominance of the (*E*) isomer.

Table 2. Hunsdiecker reaction of substituted cinnamic acids



G	R	X[a] / %	
		Br	Cl
OMe	H	95	72
Me	H	89	51
H	H	41	25
Cl	H	63	33
NO_2	H	0	0
H	Me	45[b]	31[c]

[a]Yield of pure (*E*)-2-halostyrene, based on cinnamic acid; [b]mixture of (*E*)/(*Z*) = 7:1; [c]mixture of (*E*)/(*Z*) = 2:1.

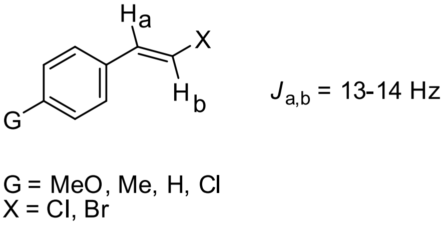


Figure 2. Typical coupling constants for the (*E*)-2-halostyrenes obtained.

The Hammett correlations[17,18] for the Hunsdiecker reactions studied (Figures 3 and 4) were determined for low conversions in competing reactions between cinnamic acid and the substituted cinnamic acid. The ratio of the formed substituted halostyrene (A_G) and halostyrene (A_H) was determined by HRGC, assuming the ratio of chromatographic areas of the reaction products is proportional to ratio of the velocity constants of their formation.

The Hammett correlation for the reactions with TCCA gave better results with σ parameter ($r^2 = 0.98$, whilst correlations with σ^+ gave $r^2 = 0.94$ and with $\sigma^{\bullet}_{JJ}$ gave $r^2 = 0.0074$)[19] and the slope $\rho = -2.6$. Figure 3 is the curve for the correlation:

$$\log (A_G/A_H) = \log (k_X/k_H) = -2.60\ \sigma \qquad (1)$$

On the other hand, the reactions with TBCA gave better results with σ^+ parameter ($r^2 = 0.99$, whilst correlations with

σ gave $r^2 = 0.93$ and with $\sigma^{\bullet}_{JJ}$ gave $r^2 = 0.0031$)[19] and the slope $\rho = -2.75$. Figure 4 is the curve for the correlation:

$$\log (A_G/A_H) = \log (k_X/k_H) = -2.75\ \sigma^+ \qquad (2)$$

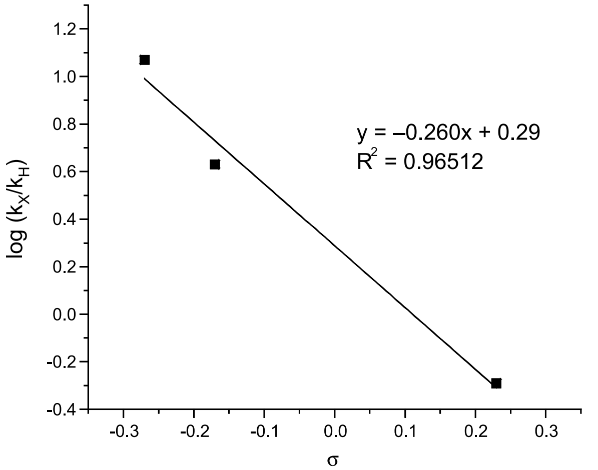


Figure 3. Hammett correlation for the Hunsdiecker reaction of cinnamic acids with TCCA.

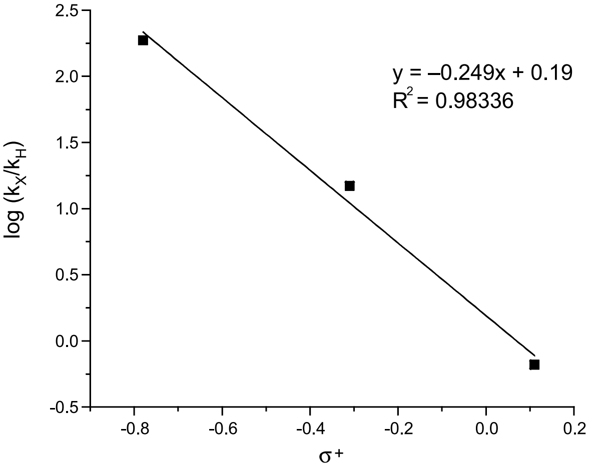


Figure 4. Hammett correlation for the Hunsdiecker reaction of cinnamic acids with TBCA.

A mechanistic pathway is proposed in Figure 5. The negative slops obtained for ρ indicate the reactions are favored by electron donating groups in the aromatic ring and thus the charge distribution in the transition state (TS) is important and characterized by an electron deficiency. Furthermore, the correlation with σ^+ values in the bromination reactions indicated that resonance effects of the substituents in the aromatic ring are more important for the stabilization of those transition states than in the chlorination reactions. Considering the values for ρ, the rate-determining step is the double bond halogenation, which can lead a halonium ion or a benzylic carbocation. In the case of the reaction with TCCA, the chloronium ion seems to be preferred, as the partial charge formed can be release by a new bond from the lone electron pair of chlorine, then justifying the best correlation with σ parameter obtained. On the other hand, the best correlation with σ^+ parameter in the reaction with TBCA indicates a more significant redistribution of the positive charge in the TS. However, the reaction parameter ρ is not high enough to support a sole formation of a benzylic carbocation.

Based on the above considerations, proposals for the TS of both reactions are shown in Figure 6. The bromonium ion has different C–Br bonds, being the benzylic carbon-bromine distance greater and hence with a partial positive charge more significant than in the case of the chloronium ion. This is due to the larger size of the bromine atom, damaging the overlapping of the orbitals responsible for the second C–Br bond. This higher carbocationic character of the intermediate favors the displacement of the equilibrium to the formation of carbocation and consequent rotation of the C–C bond, followed by decarboxylation, which explains the higher yields of the reactions performed with TBCA, compared with TCCA.

In order to better understand the reaction mechanisms, it was carried out quantum chemical calculations on these

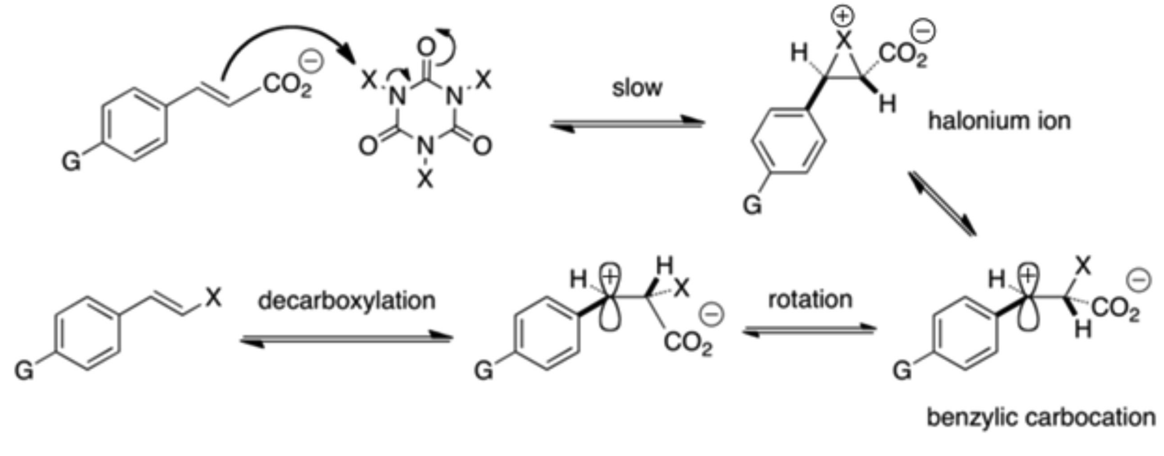


Figure 5. Mechanistic pathway proposal for the Hunsdiecker reaction of cinnamic acids with trihaloisocyanuric acids.

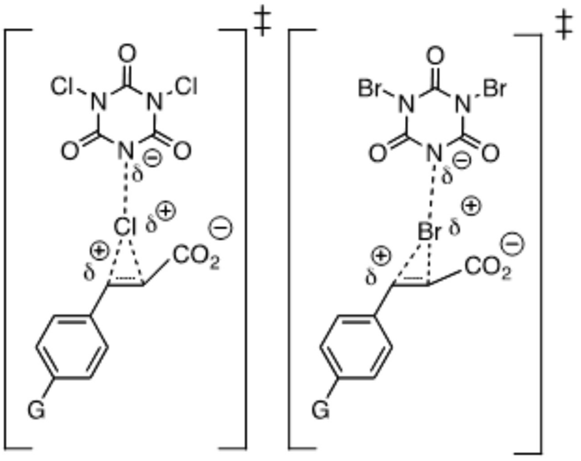


Figure 6. Proposed TS for the Hunsdiecker reactions of cinnamic acids with TCCA and TBCA.

systems at IEFPCM(H_2O)/B3LYP/6-31++G(d,p) level, for the reaction involving TCCA. The resulting optimized geometries are shown in Figure 7 and energies are shown in Table 1.

Our group started studying the formation of the π-complex between TCCA with the cinnamate anion, assuming that the acid-base reaction is faster than other chemical reactions. Thus, the reacting species would be the cinnamate anion and the reaction will take in place at the aqueous phase. In this π-complex, the distance between the nearest chlorine atom in TCCA to the double bond is 2.998 Å. This π-complex passes through a transition state that would lead to the corresponding halonium ion, with an enthalpy barrier of 3.9 kcal mol^{-1}. However, it was not possible to locate the halonium ion at this level. Instead,

Table 3. Absolute and relative energies of the species considered in this study, at IEFPCM(H_2O)/B3LYP/6-31++G** level at 298.15 K and 1 atm

Structure	–H(T) / Ha	S(T) / (cal mol^{-1} K^{-1})	–G(T) / Ha	Freq / cm^{-1}	ΔH_{rel} / (kcal mol^{-1})	ΔG_{rel} / (kcal mol^{-1})
π-Complex	2382.373225	172.638	2382.455250		0.0	0.0
Halogenation TS	2382.368906	168.768	2382.449093	-220	2.71	3.86
Product	2382.453491	195.042	2382.546162		–50.37	–57.05

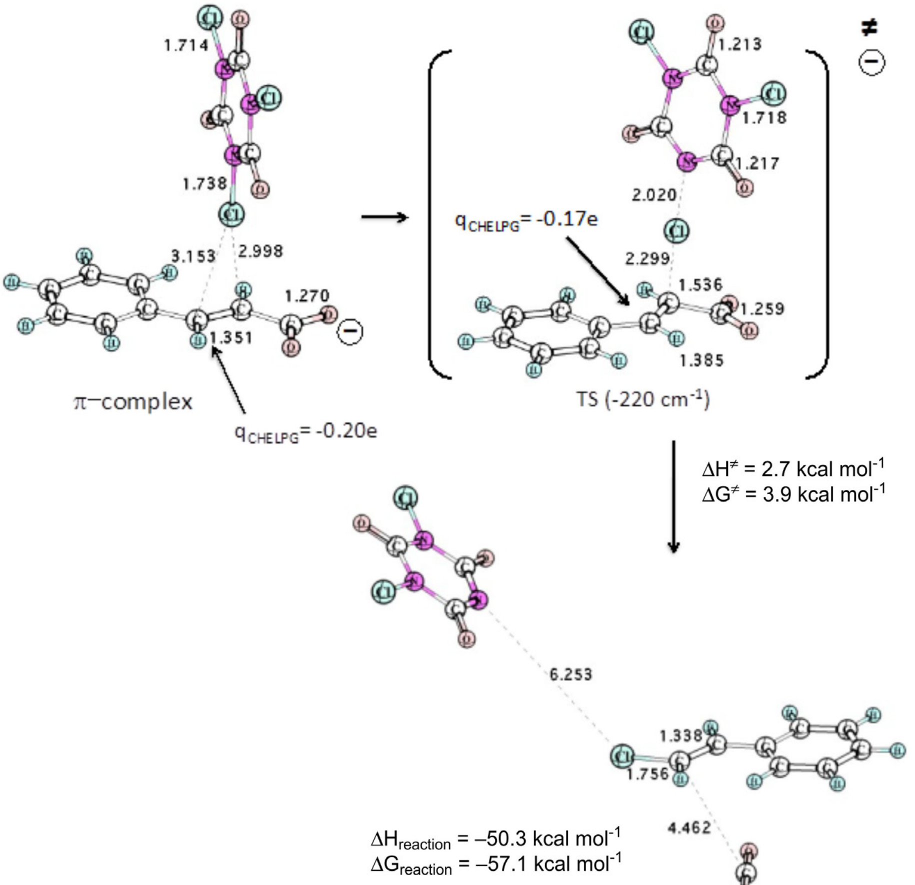


Figure 7. B3LYP/6-31++G(d,p) results for the Hunsdiecker reaction of cinnamate anion with TCCA. Interatomic distances are given in Å and energies in kcal mol^{-1}.

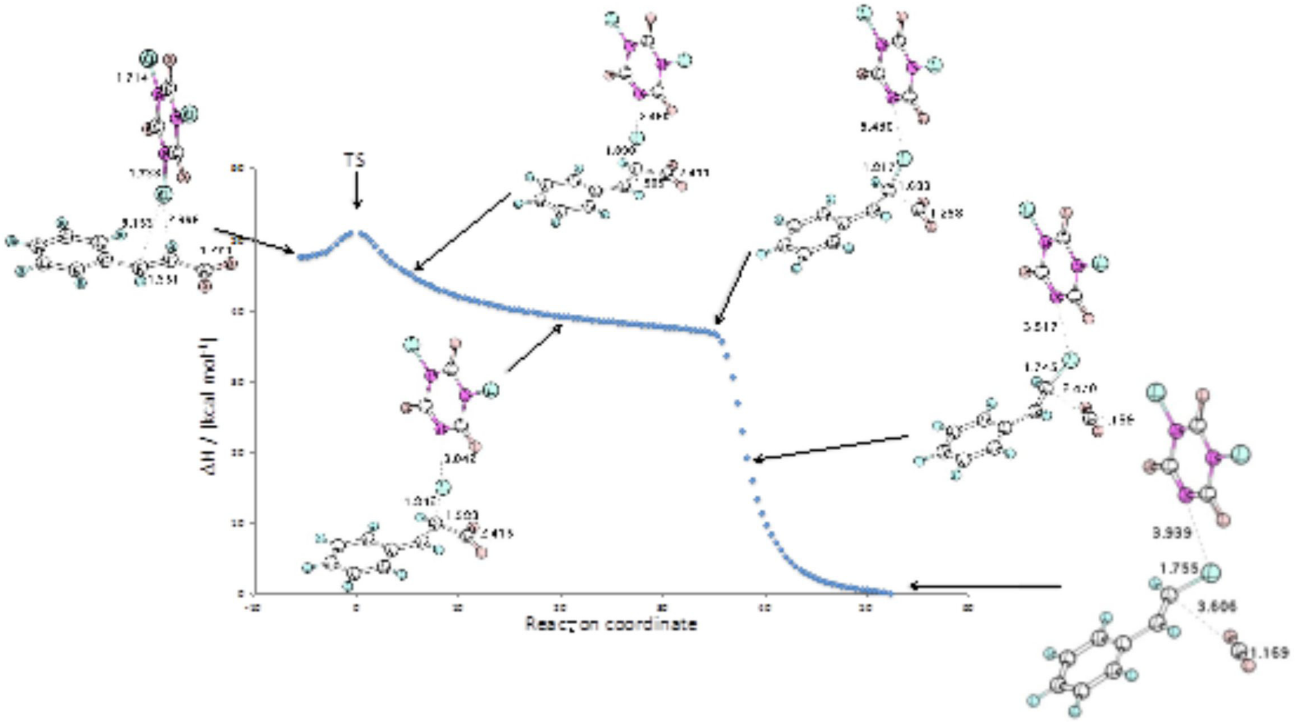


Figure 8. B3LYP/6-31++G(d,p) IRC results for reaction on cinnamate anion with TCCA.

the transition state for halogenation leads directly to the decarboxylation affording the products, as verified by IRC (intrinsic reaction coordinate) calculations, as shown in Figure 8. The reaction is exothermic by 50.4 kcal mol^{-1}.

Thus, calculations show that the barrier for the reaction is quite low, in agreement with the short reaction times for such reactions, in the order of minutes or even seconds. These theoretical results also agree with the Hammett experiments since it also predicts that the rate-controlling step for the process involves the development of positive charge on the atom bonded to the aromatic ring (Figure 6). It was calculated this developing charge at benzylic carbon atom as

$$\delta^+ = (\text{charge in the TS} = -0.1735\ e) - (\text{charge in the reactants} = -0.2057\ e) \qquad (3),$$

using CHelpG scheme[20] for computing atomic charges. The developing charge was computed to be $\delta^+ = +0.0322$ e, thus being positive in agreement with the Hammett data.

Conclusion

In summary, trihaloisocyanuric acids react with cinnamic acids to produce (*E*)-2-halostyrenes in a biphasic system (H_2O/Et_2O), through an electrophilic rate controlling mechanism. This new methodology is very attractive from the green chemistry point of view as it avoids the use of halogenated solvents, corrosive and toxic molecular halogens and harmful heavy metal salts.

Experimental

General information

Trichloroisocyanuric acid (commercial grade, 98%), cinnamic acids (Aldrich) and other chemicals and solvents were used as received. Tribromoisocyanuric acid was prepared as described.[11] The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200 (200 MHz and 50 MHz, respectively) spectrometer in $CDCl_3$ solutions with TMS (tetramethylsilane) as internal standard. HRGC analyses were performed on a HP-5890-II gas chromatograph with FID (flame ionization detector) using a 30 m (length), 0.25mm (ID) and 25 µm (phase thickness) RTX-5 capillary column and H_2 (flow rate 50 cm s^{-1}) as carrier gas (split: 1:10). 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.

Typical Hunsdiecker reaction of cinnamic acids with trihaloisocyanuric acids

Et_2O (20 ml) and the trihaloisocyanuric acid (1.67 mmol) were added to a solution of cinnamic acid (5 mmol) in 2% aqueous NaOH (20 ml). After stirring for 24 h, the organic layer was separated and evaporated to give the pure 2-halostyrene.

(*E*)-*2*-Chlorostyrene

^{1}H NMR (200 MHz, CDCl$_3$) δ 6.66-6.60 (d, 1H, *J* 13.67 Hz), 6.87-6.80 (d, 1H, *J* 13.67 Hz), 7.25-7.33 (m, 10H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 118.9, 126.3, 128.4, 129.0, 133.5, 135; MS (70 eV) *m/z* 140 (M$^+$ + 2), 138 (M$^+$), 103 (100%), 77, 51.

(*E*)-*2*-Bromostyrene

^{1}H NMR (200 MHz, CDCl$_3$) δ 6.72-6.79 (d, 1H, *J* 13,99 Hz), 7.06-7.13 (d, 1H, *J* 13,99 Hz), 7.29 (m, 5H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 106.7, 126.3, 128.5, 129.0, 136.1, 137.4; MS (70 eV) *m/z* 184 (M$^+$ + 2), 182 (M$^+$), 103 (100%), 77, 51.

(*E*)-*2*-Chloro-*p*-methoxystyrene

^{1}H NMR (200 MHz, CDCl$_3$) δ 3.77 (s, 3H), 6.50-6.43 (d, 1H, *J* 13.62 Hz), 6.78-6.71 (d, 1H, *J* 13.67 Hz), 6.85-6.81 (d, 2H), 7.22-7.17 (d, 2H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 55.4, 114.4, 116.5, 127.5, 127.8, 132.9, 159,8; MS (70 eV) *m/z* 170 (M$^+$ + 2), 168 (M$^+$, 100%), 153, 125, 89.

(*E*)-*2*-Bromo-*p*-methoxystyrene

^{1}H NMR (200 MHz, CDCl$_3$) δ 3.80 (s, 3H), 6.63-6.56 (d, 1H, *J* 13.94 Hz), 6.87-6.83 (d, 2H), 7.07-7.00 (d, 1H, *J* 13.95 Hz), 7.25-7.20 (d, 2H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 55.5, 104.2, 114.4, 127.6, 129.0, 136.8, 159.9; MS (70 eV) *m/z* 214 (M$^+$ + 2), 212 (M$^+$, 100%), 199, 197, 133, 118, 90.

(*E*)-*2*-Chloro-*p*-methylstyrene

^{1}H NMR (200 MHz, CDCl$_3$) δ 2.33 (s, 3H), 6.60-6.54 (d, 1H, *J* 13.66 Hz), 6.83-6.76 (d, 1H, *J* 13.66 Hz), 7.24-7.09 (m, 4H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 21.4, 117.9, 126.2, 129.7, 132.3, 133.3, 138.3; MS (70 eV) *m/z* 154 (M$^+$ + 2), 152 (M$^+$), 117 (100%), 115, 91.

(*E*)-*2*-Bromo-*p*-methylstyrene

^{1}H NMR (200 MHz, CDCl$_3$) δ 2.32 (s, 3H), 6.73-6.66 (d, 1H, *J* 13.96 Hz), 7.10-7.03 (d, 1H, *J* 13.89 Hz), 7.24-7.14 (m, 5H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 21.5, 105.6, 126.2, 129.7, 133.4, 137.3, 138.4; MS (70 eV) *m/z* 198 (M$^+$ + 2), 196 (M$^+$), 117, 115 (100%), 91

(*E*)-*2*-Chloro-*p*-chlorostyrene

^{1}H NMR (200 MHz, CDCl$_3$) δ 6.66-6.59 (d, 1H, *J* 13.69 Hz), 6.83-6.76 (d, 1H, *J* 13.70 Hz), 7.32-7.20 (m, 5H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 119.6, 127.5, 129.2, 132.4, 133.6, 134.2; MS (70 eV) *m/z* 176 (M$^+$ + 4), 174 (M$^+$ + 2), 172 (M$^+$), 137 (100%), 102, 101, 75.

(*E*)-*2*-Bromo-*p*-chlorostyrene

^{1}H NMR (200 MHz, CDCl$_3$) δ 6.79-6.72 (d, 1H, *J* 14.01 Hz), 7.09-7.02 (d, 1H, *J* 14.03 Hz), 7.32-7.19 (m, 4H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 107.4, 127.5, 129.2, 134.3, 134.6, 136.2; MS (70 eV) *m/z* 220 (M$^+$ + 4), 218 (M$^+$ + 2), 216 (M$^+$), 137 (100%), 102, 101, 75.

Computational details

All calculations were carried out using the B3LYP functional and 6-31++G** basis set. Minima on the potential energy surface were characterized by absence of the harmonic frequencies of the respective optimized structures, while the transition state presents a single imaginary frequency after vibrational analysis. Further IRC analysis confirmed that the transition state connects the π-complex to the final decarboxylated products. All energy differences correspond to enthalpy differences at 298.15 K and 1 atm. The calculations include solvation using the IEFPCM(H$_2$O) model.[21] All calculations were carried out using the Gaussian 09 package.[22]

Acknowledgments

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