EXPLORING THE SUBSTRATE SCOPE OF THE RU(II)-CATALYZED KHARASCH REACTION

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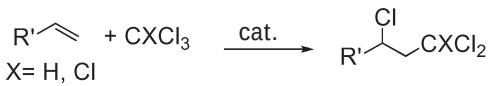
Dedicated to Professor Štefan Toma on the occasion of his 70th birthday.

The Kharasch reaction, or atom-transfer addition of polyhalogenated alkanes to alkenes is known to be catalyzed by a number of Ru(II) complexes. The easily prepared $[RuCl_2(PPh_3)_3]$ was used to investigate the reaction scope. A number of halogenated alkanes were added to a range of alkenes with good to excellent regioselectivities.
Keywords: Atom transfer; Ruthenium; Alkenes; Catalysis; Additions; Polyhalogenated alkanes.

The atom-transfer addition of polyhalogenated alkanes to alkenes (Scheme 1), the Kharasch addition[1], is an important tool in organic chemistry, because the resulting products may be transformed into a variety of functional groups[2,3]. In principle, this process benefits from the chemical efficiency; no chemical waste-products are formed[4].



SCHEME 1
General catalytic Kharasch addition of a chloroalkane to an alkene

Several transition metal complexes have been shown to catalyze the *anti*-Markovnikov addition of polyhalogenated compounds to alkenes[2]. Typical drawbacks of the Kharasch addition are the limited scope of halogenated substrates and comparatively harsh reaction conditions. Several successful efforts in overcoming these problems have been published. Im-

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portant among them is the $[RuCl_2(PPh_3)_3]$ catalyzed reaction, first reported by Nagai et al.[5], which has been applied to a variety of synthetically useful reactions[6]. In a more recent publication, Noels et al. demonstrated that $[Cp^*RuCl(PPh_3)_3]$ was extremely active in catalyzing the addition of CCl_4 and $CHCl_3$ to various alkenes, achieving turnover numbers (TONs) of 1600–1700 at temperatures as low as 40 °C [7]. To date, a number of Ru(II) catalysts have been reported possessing superior performance superior to $[RuCl_2(PPh_3)_3]$ [8–10].

The ruthenium-catalyzed Kharasch reaction is believed to proceed via a radical mechanism in the coordination sphere of the metal complex[2]. In the case of $[RuCl_2(PPh_3)_3]$, the active catalyst is believed to be the fourteen-electron species $[RuCl_2(PPh_3)_2]$, generated by the dissociation of one PPh_3 ligand[11].

To date there have been few reports in the literature that have dealt with the scope and limitations of the Ru-catalyzed Kharasch addition reaction. We therefore became interested in investigating the reaction scope with respect to alkenes and halogen sources. Especially interesting is the addition of α-halo ketones and esters to unsymmetrical olefins, potentially leading to high regiospecificity in the addition product.

RESULTS

In the first set of experiments, we investigated the $[RuCl_2(PPh_3)_3]$ (**1**) catalyzed addition of CCl_4 (**2**) to various alkenes (Table I). We preferred the $[RuCl_2(PPh_3)_3]$ complex to $[Cp^*RuCl(PPh_3)_3]$ due to its easy preparation[12]. After refluxing a mixture of alkene and CCl_4 in benzene with 1 mole % of $[RuCl_2(PPh_3)_3]$ for 24 h, the addition products **16**–**28** were obtained in moderate to excellent yields. As indicated in Table I, the regiospecificity of the addition product varies from good to excellent. In the case of terminal olefins (Table I, entries 1, 2, 13), preferential addition of the Cl atom to the most substituted position of the double bond was observed. With α,β-unsaturated alkenes and CCl_4, the Cl atom was preferentially transferred to the benzylic carbon. Addition of CCl_4 to cyclic alkenes resulted in the exclusive formation of the *trans* product (Table I, entries 4–7).

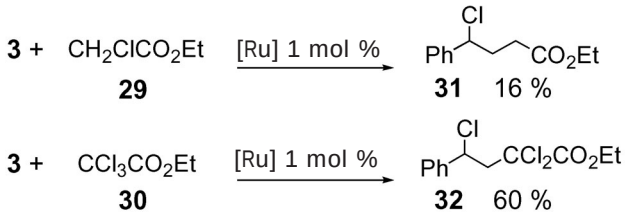
We then further investigated the scope of this system with the addition of ethyl chloroacetate (**29**) and ethyl trichloroacetate (**30**) to styrene (**3**). As shown in Scheme 2, the reaction proceeded faster with the more halogenated ester **30** giving 60% yield (compared to only 16% for **29** in 24 h). Using the same reaction conditions, we added **30** to a number of alkenes **4**, **6**, **8**, **11**–**15** (Table II). The same regioselectivity pattern was observed using

TABLE I
Ru(II)-catalyzed addition of CCl_4 to various alkenes

Entry	Alkene	Product[a]	Regioselectivity[b]	Conversion[b] (Yield), %
1	 **3**	 **16**	>99:1	81 (80)
2	 **4**	 **17**	>99:1	67 (65)
3	 **5**	 **18**	–	93 (90)
4	 **6**	 **19**	–	81 (79)
5	 **7**	 **20**	–	54 (50)
6	 **8**	 **21**	–	70 (61)
7	 **9**	 **22**	>99:1	71 (67)
8	 **10**	 **23**	87:13	30 (23)
9	 **11**	 **24**	64:36	13 (10)
10	 **12**	 **25**	>99:1	53 (50)
11	 **13**	 **26**	89:11	44 (42)
12	 **14**	 **27**	91:9	56 (52)
13	 **15**	 **28**	>99:1	92 (91)

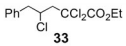
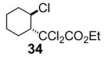
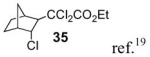
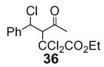
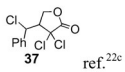
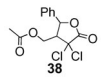
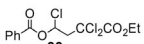
[a] Only the major isomer is shown, ^{1}H NMR analysis suggests predominant *trans* diastereomer in all cases; compounds **16** [16], **17** [17], **18** [18], **19** [18], **20** [19], **21** [20], **26** [21]. [b] Determined by ^{1}H NMR.

30 (Table II) as with CCl_4, the conversions for the addition of **30**, however, were generally lower than for the addition of CCl_4.



SCHEME 2
$[RuCl_2(PPh_3)_3]$-catalyzed addition of **29** and **30** to **3**. Conditions: $[RuCl_2(PPh_3)_3]$ 1 mol %, C_6H_6, 75 °C, 24 h; compound **32** [15]

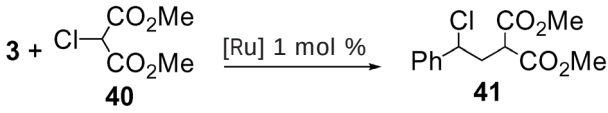
TABLE II
Addition of **30** to alkenes **4**, **6**, **8**, **11**–**15**

Entry	Alkene	Product[a]	Regioselectivity[c]	Conversion[c] (Yield), %
1a			>99:1	62 (60)
2			–	68 (63)
3		 ref.[19]	–	96 (94)
4			>99:1	30 (26)
5		 ref.[22c]	–	69 (61)
6			–	58 (52)
7			>99:1	36 (33)

[a] In 1,4-dioxane. [b] Only the major isomer is shown, ^{1}H NMR analysis suggests predominant *trans* diastereomer in all cases. [c] Determined by ^{1}H NMR.

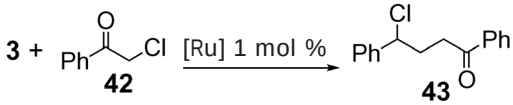
Of interest is the reaction of **30** with cinnamyl acetate (Table II, entry 6) which resulted in no linear addition product. Rather a two-step reaction occurred, forming lactone **38** as the only product. This is in agreement with previous findings[13–15]. Similar lactone formation was also observed for the addition of **30** to cinnamyl alcohol (Table II, entry 6).

With successful results from the addition of α-halogenated monoesters, we proceeded to investigate the addition of dimethyl chloromalonate (**40**) to **3**. The addition proceeded rather slowly, giving only 15% yield after 24 h (Scheme 3).



SCHEME 3
[$RuCl_2(PPh_3)_3$]-catalyzed Kharasch addition of **40** to **3**. Conditions: [$RuCl_2(PPh_3)_3$] 1 mol %, C_6H_6, 75 °C, 24 h

The slow reaction observed in this case indicates that an important factor for obtaining high conversions under the conditions used is the level of halogenation in the halogen source. Phenacyl chloride (**42**) was also successfully added to **3**, although the product **43** was formed in a low yield, 18% (Scheme 4).



SCHEME 4
Addition of **42** to **3**. Conditions: [$RuCl_2(PPh_3)_3$] 1 mol %, C_6H_6, 75 °C, 24 h; compound **43** [23]

CONCLUSIONS

We have investigated the scope and limitations of the alkenes that can be used for this addition, and shown that [$RuCl_2(PPh_3)_3$] catalyzes the addition of various halogen sources to a broad range of alkenes, producing substrates of high synthetic value which can be further utilized. We have shown that the Ru(II)-catalyzed Kharasch addition to alkenes need not be restricted to the usual polyhalogenated compounds, CCl_4 and ethyl trichloroacetate, as malonate esters and phenacyl chloride can also be used as reactants for this reaction.

EXPERIMENTAL

All substrates were purchased from commercial sources and used as received. All reactions were conducted under nitrogen with magnetic stirring. ^{1}H and ^{13}C NMR spectra (δ, ppm; *J*, Hz) were recorded in $CDCl_3$ (7.26 ppm ^{1}H, 77.0 ppm ^{13}C), on a Varian Unity 400 spectrometer at 400 and 100.6 MHz, respectively. Infrared spectra (ν_{max}, cm^{-1}) were recorded on a Perkin–Elmer 1760 FT-IR spectrometer. For column chromatography, Merck silica gel 60 (230–400 mesh) was used.

General Procedure

The catalyst (1 mol %) was weighed in a 10-ml round-bottom flask to which the alkene (2 mmol) dissolved in benzene (0.5 ml) was added. The chlorinated compound (10 mmol) was added via syringe and the reaction mixture was stirred at 75 °C for 24 h. The reaction mixture was cooled to room temperature and the solvent evaporated in vacuo. The resulting crude product was purified by flash chromatography. Compounds **16**–**21**, **26**, **32**, **35**, **37**, and **43** were characterized by comparison of their spectral data with those in the literature.

2-Chloro-3-(trichloromethyl)cyclohexan-1-one (**22**). ^{1}H NMR ($CDCl_3$): 1.61–1.73 (m, 1 H, CH_2); 2.19–2.27 (m, 1 H, CH_2); 2.33–2.42 (m, 3 H, CH_2); 2.88–2.92 (m, 1 H, CH_2); 3.09 (dt, 1 H, *J* = 14.2, 7.0, $CHCCl_3$); 4.84 (d, 1 H, *J* = 2.4, -CHCl). ^{13}C NMR ($CDCl_3$): 22.3, 23.3, 34.6, 60.4, 60.8, 95.3, 146.1. IR (neat): 3437 (w), 2956, 2875, 1726 (s), 1449, 1425, 945, 815, 781, 754. MS (EI), *m/z* (%): 249.9 (100) $[M]^+$, 248.3 (93), 252.1 (47), 254.1 (34), 251.3 (7), 253.2 (5).

[1,3,3,3-Tetrachloro-2-(chloromethyl)propyl]benzene (**23**). ^{1}H NMR ($CDCl_3$): 3.48–3.51 (m, 1 H, $CHCCl_3$); 4.12 (dd, 1 H, *J* = 12.6, 3.3, CH_2); 4.28 (dd, 1 H, *J* = 12.6, 5.4, CH_2); 5.85 (d, 1 H, *J* = 2.4, -CHCl); 7.35–7.45 (m, 3 H, Ar-H); 7.57 (d, 2 H, *J* = 7.6, Ar-H). ^{13}C NMR ($CDCl_3$): 40.8, 61.3, 67.7, 100.5, 127.5, 128.8, 129.0, 139.8. IR (neat): 1495, 1451, 1439, 823, 765, 717, 696 (s). MS (EI), *m/z* (%): 305.9 (100) $[M]^+$, 307.9 (71), 303.8 (57), 309.9 (17), 308.9 (13), 307.0 (9), 304.9 (7), 311.1 (5).

4-Chloro-4-phenyl-3-(trichloromethyl)butan-2-one (**24**). ^{1}H NMR ($CDCl_3$): 2.59 (s, 3 H, Me); 4.36 (d, 1 H, *J* = 10, $CHCCl_3$); 5.50 (d, 1 H, *J* = 10, CHCl); 7.32–7.37 (m, 3 H, Ar-H); 7.47–7.50 (m, 2 H, *J* = 7.6, Ar-H). ^{13}C NMR ($CDCl_3$): 34.0, 61.5, 73.2, 99.3, 128.8, 129.0, 129.7, 137.6, 200.9. IR (neat): 3447 (w), 1730 (s), 1456, 1356, 1290, 1246, 813, 760, 712 (s), 696. MS (EI), *m/z* (%): 300.0 (100) $[M]^+$, 298.1 (93), 302.0 (88), 301.0 (22), 304.1 (12), 298.9 (9), 302.9 (4), 305.0 (1).

3-Chloro-3-phenyl-2-(trichloromethyl)propan-1-ol (**25**). ^{1}H NMR ($CDCl_3$): 1.97 (brs, 1 H, OH); 3.33–3.36 (m, 1 H, -$CHCCl_3$); 4.35 (dd, 1 H, *J* = 12.7, 3.9, -CH_2); 4,43 (dd, 1 H, *J* = 12.7, 5.3, -CH_2); 5.79 (d, 1 H, *J* = 2.4, -CHCl); 7.35–7.45 (m, 3 H, Ar-H); 7.57 (d, 2 H, *J* = 7.5, Ar-H). ^{13}C NMR ($CDCl_3$): 61.9, 62.0, 66.6, 100.8, 127.5, 128.8, 129.2, 140.8. IR (neat): 3414 (br), 1495, 1450, 1041 (s), 908, 698 (s), 731, 697. MS (EI), *m/z* (%): 288.0 (100) $[M]^+$, 286.2 (91), 290.4 (73), 289.0 (30), 292.0 (12), 287.2 (8), 291.1 (6), 292.0 (1).

3-Chloro-3-phenyl-2-(trichloromethyl)acetate (**27**). ^{1}H NMR ($CDCl_3$): 1.84 (s, 3 H, H_3C-C(=O)OC-); 3.44–3.47 (m, 1 H, -$CHCCl_3$); 4.76–4.79 (m, 2 H, -CH_2OC(=O)-); 5.89 (d, 1 H, *J* = 2.1, PhCHClC); 7.34–7.38 (m, 1 H, Ar-H); 7.41–7.45 (m, 2 H, Ar-H); 7.51–7.56 (m, 2 H, Ar-H). ^{13}C NMR ($CDCl_3$): 20.8, 60.9, 61.9, 63.7, 100.1, 127.2, 128.5, 128.6, 140.1, 170.4. IR (neat): 1743, 1225, 1042, 762, 697. MS (EI), *m/z* (%): 329.6 (100) $[M]^+$, 327.96 (88), 330.9 (56), 330.7 (38), 334.1 (31), 329.6 (10), 333.4 (6), 335.0 (3).

1,3,3,3-Tetrachloropropyl benzoate (**28**). ^{1}H NMR ($CDCl_3$): 3.58 (dd, 1 H, *J* = 15.5, 2.3, CH_2CCl_3); 3.81 (dd, 1 H, *J* = 15.5, 8.6, CH_2CCl_3); 7.16–7.18 (dd, 1 H, *J* = 8.6, 2.3, -CHCl); 7.50–7.53 (m, 2 H, Ar-H); 7.65–7.66 (m, 1 H, Ar-H); 8.13–8.15 (m, 2 H, Ar-H). ^{13}C NMR ($CDCl_3$): 61.2, 79.9, 94.3, 128.5, 128.9, 130.5, 134.4, 163.8. IR (neat): 1741, 1242, 1062, 1045, 701, 573. MS (EI), *m/z* (%): 301.0 (100) $[M]^+$, 299.9 (78), 304.2 (37), 302.8 (17), 305.4 (11), 301.0 (9), 305.0 (4).

Ethyl 4-chloro-4-phenylbutanoate (**31**). ^{1}H NMR ($CDCl_3$): 1.29 (t, 3 H, *J* = 7.2, $H_3CH_2OC(=O)$); 2.39–2.44 (m, 2 H, $-CH_2C(=O)O-$); 2.49–2.53 (m, 2 H, $-CH_2CHClPh$); 4.16 (q, 2 H, *J* = 7.2, $CH_3CH_2OC(=O)-$); 4.99 (dd, 1 H, *J* = 8.5, 6.2, PhCHCl-); 7.34–7.43 (m, 5 H, Ar-H). ^{13}C NMR ($CDCl_3$): 14.5, 31.9, 35.3, 60.8, 62.9, 127.1, 128.7, 129.0, 141.3, 172.8. IR (neat): 1729, 1180, 1157, 761, 696. For $C_{12}H_{15}Cl_1O_2$ (226.7) calculated: 63.58% C, 6.67% H; found: 63.66% C, 6.56% H.

Ethyl 2,2,4-trichloro-5-phenylpentanoate (**33**). ^{1}H NMR ($CDCl_3$): 1.39 (t, 3 H, *J* = 7.1, CH_3CH_2-OC(=O)-); 2.89 (dd, 1 H, *J* = 15.1, 3.2, $PhCH_2$-CHCl); 3.12–3.17 (m, 3 H, $PhCH_2CHCl$-, $-CH_2CCl_2$-); 4.35 (q, 2 H, *J* = 7.1, CH_3CH_2-OC(=O)-); 4.45 (m, 1 H, $-CHClCH_2$-); 7.26–7.27 (m, 2 H, Ar-H); 7.31–7.33 (m, 1 H, Ar-H); 7.36–7.40 (m, 2 H, Ar-H). ^{13}C NMR ($CDCl_3$): 14.0, 45.3, 52.1, 58.3, 64.4, 83.0, 127.5, 128.9, 129.6, 136.9, 165.7. IR (neat): 1758, 1745, 1242, 1200, 1027, 750, 698. MS (EI), *m/z* (%): 313 (27), 311 (82), 310 (20), 309 (94) $[M]^+$, 275 (37), 273 (59), 239 (19), 238 (40), 237 (53), 236 (100), 209 (23). For $C_{13}H_{15}Cl_3O_2$ (309.6) calculated: 50.43% C, 4.88% H; found: 51.47% C, 4.98% H.

Ethyl 2,2-dichloro-2-(2-chlorocyclohexyl)acetate (**34**). ^{1}H NMR ($CDCl_3$): 1.35–1.46 (m, 6 H, CH_2, CH_2CH_3); 1.71–1.85 (m, 2 H, CH_2); 1.89–1.93 (m, 1 H, CH_2); 2.24–2.30 (m, 1 H, CH_2); 2.57–2.62 (m, 1 H, CH_2); 2.80–2.87 (m, 1 H, $CHCCl_2$); 3.99 (ddd, 1 H, *J* = 10.1, 5.9, 4.2, CHCl); 4.27–4.40 (m, 2 H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): 13.9, 25.0, 26.5, 28.2, 37.9, 54.7, 64.1, 166.6. IR (neat): 3506 (w), 2940, 1761 (s), 1745, 1451, 1252, 1228 (s), 1023, 911, 732 (s). MS (EI), *m/z* (%): 272.2 (100), 274.1 (79) $[M]^+$, 276.2 (67), 273.1 (14), 275.0 (12), 277.2 (4), 278.3 (3).

Ethyl 2,2-dichloro-3-[chloro(phenyl)methyl]-4-oxopentanoate (**36**). ^{1}H NMR ($CDCl_3$): (t, 3 H, *J* = 7.1, CH_2CH_3); 2.57 (s, 3 H, $CH_3C(=O)-$); 3.75 (q, *J* = 7.1, CH_2CH_3); 4.53 (d, 1 H, *J* = 9.6, -CH); 5.45 (d, 1 H, *J* = 9.6, PhCHCl); 7.33–7.39 (m, 4 H, Ar-H); 7.46–7.49 (m, 1 H, Ar-H). ^{13}C NMR ($CDCl_3$): 13.7, 34.1, 60.8, 64.5, 65.1, 81.9, 128.5, 129.3, 129.6, 137.9, 164.0, 202.2. IR (neat): 2986 (w), 1763, 1726 (m), 1247, 1029, 907, 726 (s), 695. MS (EI), *m/z* (%): 336.0 (100), 338.0 (91) $[M]^+$, 340.0 (29), 337.0 (17), 339.0 (14), 341.0 (5), 342.1 (4).

4,4-Dichloro-5-oxo-2-phenyltetrahydrofuran-3-yl methylacetate (**38**). ^{1}H NMR ($CDCl_3$): 1.86 (s, 3 H, $CH_3C(=O)-$); 3.33–3.35 (m, 1 H, $-CHCCl_2$-); 4.49 (dd, 1 H, *J* = 12.0, 6.2, acetate-CH_2-); 4.56 (dd, 1 H, *J* = 12.0, 7.0, acetate-CH_2-); 5.24 (d, 1 H, *J* = 9.8, PhCHCl); 7.38–7.40 (m, 2 H, Ar-H); 7.47–7.48 (m, 3 H, Ar-H). ^{13}C NMR ($CDCl_3$): 20.5, 31.2, 57.8, 59.6, 81.6, 127.3, 129.4, 130.4, 134.2, 166.8, 170.5. IR (neat): 1799, 1742, 1225, 1184, 1044, 964, 770, 692. MS (EI), *m/z* (%): 305 (30), 304 (7), 303 (44) $[M]^+$, 235 (7), 209 (34), 208 (13), 207 (100), 179 (15).

1,3,3-Trichloro-4-ethoxy-4-oxobutyl benzoate (**39**). ^{1}H NMR ($CDCl_3$): 1.30 (t, 3 H, *J* = 7.1, CH_3CH_2-OC(=O)-); 3.32 (dd, 1 H, *J* = 15.1, 3.3, $-CH_2CCl_2$-); 3.65 (dd, 1 H, *J* = 15.1, 8.7, $-CH_2CCl_2$-); 4.23–4.29 (m, 2 H, $CH_3CH_2OC(=O)-$); 7.06 (dd, 1 H, *J* = 8.7, 3.3, CHCl); 7.49–7.52 (m, 2 H, Ar-H); 7.64–7.65 (m, 1 H, Ar-H); 8.07–8.08 (m, 2 H, Ar-H). ^{13}C NMR ($CDCl_3$): 13.9, 52.1, 64.6, 77.3, 80.1, 128.5, 128.9, 130.4, 134.4, 163.7, 165.7. IR (neat): 1742, 1243, 1052, 1082, 1023, 706, 684. MS (EI), *m/z* (%): 343 (13), 342 (7), 341 (42), 340 (11), 339 (53) $[M]^+$, 307 (6), 306 (5), 305 (31), 304 (9), 303 (52), 105 (100). For $C_{13}H_{13}Cl_3O_4$ (339.6) calculated: 45.98% C, 3.86% H; found: 47.25% C, 4.11% H.

Dimethyl 2-(2-chloro-2-phenylethyl)malonate (**41**). ^{1}H NMR ($CDCl_3$): 2.67 (m, 2 H, $CHClCH_2$-); 3.70 (dd, 1 H, *J* = 8.0, 6.9, -CHC(=O)-); 3.78 (s, 3 H, CH_3OCO-); 3.79 (s, 3 H, CH_3OC(=O)-); 4.97 (dd, 1 H, *J* = 8.0, 6.8, PhCHCl-); 7.57–7.69 (m, 5 H, Ar-H). ^{13}C NMR ($CDCl_3$): 39.0, 49.7, 53.0, 53.1, 61.1, 127.2, 128.9, 129.0, 140.7, 169.2, 169.4. IR (neat): 1732, 1435, 1269, 1221, 1152, 697. MS (EI), *m/z* (%): 274 (4), 273 (26), 272 (15), 271 (100) $[M]^+$, 238 (9), 236 (100), 235 (11), 232 (22).

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