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DICHOTOMOUS REACTIVITY OF PCl_5 AND PBr_5 TOWARD CYCLIC KETONES: A ONE-STEP PREPARATION OF 1,1,2-TRICHLOROCYCLOALKANES

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Abstract: Small-ring cyclic ketones react with excess PCl_5 in CCl_4 (reflux, 1-3 d) to give the corresponding 1,1,2-trichlorocycloalkanes, but react with PBr_5 to give ketones brominated in the α-positions.

Reaction of carbonyl compounds with PCl_5 is a well-known route to vinyl chlorides and *gem*-dichlorides; these reactions are usually done with 1-2 equiv of PCl_5 at or near 0°.[1,2] We now report (Table and eq 1) that treatment of simple small-ring cyclic ketones **1**

(*) To whom correspondence should be addressed. This paper is dedicated to Professor Robert W. Gleason on the occasion of his retirement.

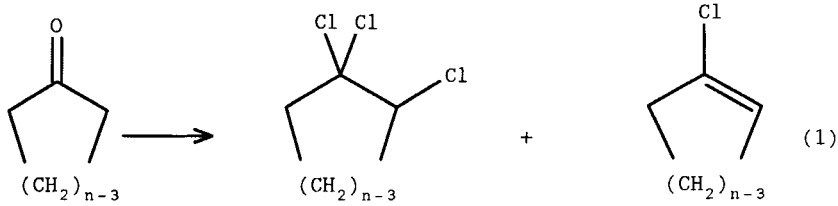
Table

	Sub.[a]	PX_5(eq)	Sol.[b]	T[c]	t[d]	Products(%)[e]
1	**1a**	Cl(3.4)	CCl_4	Rf.	72	**2a**(75)
2	**1b**	Cl(3.4)	CCl_4	Rf.	72	**2b**(74)
3	**1c**	Cl(3.1)	CCl_4	Rf.	24	**2c**(66)
4	**1d**	Cl(3.4)	CCl_4	Rf.	24	**2d**(66)
5	**1e**	Cl(3.4)	CCl_4	Rf.	24	**3e**(64)
6	**3e**	Cl(3.3)	CCl_4	Rf.	120	**2e**(75)
7	**1c**	Cl(1.5)	CCl_4	Rf.	18	**2c**(16), **3c**(31)[f]
8	*g*	Cl(3)	CCl_4	Rf.	18	**2c**(27 from **1c**)
9	**1e**	Br(2.0)	CCl_4	Rf.	72	**4e**(78)[h]
10	**1d**	Br(2.0)	CCl_4	Rf.	72	**4d**(34)
11	**1c**	Br(3.4)	CCl_4	Rf.	2	*trans*-**4c**(~32), *cis*-**4c**(~10), **5c**(~28)[f]
12	**1b**	Br(2.3)	$CHCl_3$	-46	0.5	See text

a) Substrate. *b*) Solvent. *c*) Temperature (Rf. denotes reflux; numerical values in °C). *d*) Time (h). *e*) Isolated yields except where noted. *f*) Yields estimated by ^{1}H NMR. *g*) Mixture from entry 7. *h*) 95:5 *trans:cis*.[f,6]

with *3-4 equiv of* PCl_5 *in* CCl_4 *at reflux for 1-3 d* gives 1,1,2-trichlorocycloalkanes (**2**) in 64-75% yields.[3,4] Previously reported routes to 1,1,2-trichlorocycloalkanes involve either separation of mixtures or pregeneration of enol derivatives;[5] by contrast, the new reaction gives compounds **2** in one step without isolation of intermediates.

Yields of trichlorides **2** were essentially independent of ring size and reaction time in the ranges 4-7 carbons and 1-3 d (Table, entries 1-4). Reaction of



(1)

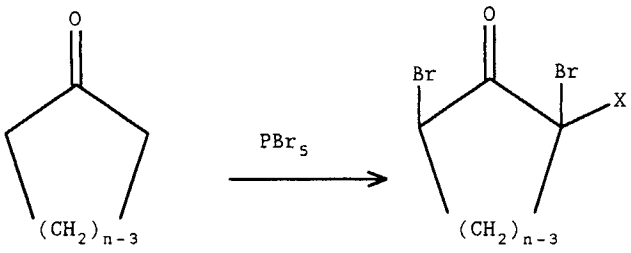
1 2 3

a: n = 4; b: n = 5; c: n = 6; d: n = 7; e: n = 8

cyclooctanone **(1e)** was slower, and led after 24 h to 1-chlorocyclooctene (**3e**; entry 5); resubmission of **3e** to PCl_5 (5 d) gave a product which we could not obtain analytically pure, but whose IR and 360-MHz ^1H NMR spectra are consistent with structure **2e** (entry 6). Vinyl chlorides **3** were also obtained if the system was starved for PCl_5 (entry 7): with only 1.5 equiv of PCl_5, cyclohexanone **(1c)** gave a mixture of **2c** and 1-chlorocyclohexene (**3c**). Resubmission of this mixture to PCl_5 (entry 8) gave **2c**.

Formally analogous treatment of **1b-e** with PBr_5 (entries 9-12) gave neither 1,1,2-tribromocycloalkanes nor 1-bromocycloalkenes, but led to α,α'-brominated ketones **4** and **5** (eq 2). Dibromoketones **4e** and **4d** were obtained in moderate yields from **1e** and **1d** respectively (entries 9 and 10).

By contrast, yields of products from **1c** or **1b** and PBr_5 were very low unless the usual base wash was excluded from the workup; α-brominated cyclohexanones and



(2)

1

4: X = H
5: X = Br

b: n = 5; c: n = 6; d: n = 7; e: n = 8

cyclopentanones are notoriously sensitive to base.[7] The mixture of products from **1c** and PBr_5 (entry 11) could not be separated chromatographically, and decomposed upon attempted fractional distillation; its NMR spectra led to its assignment as a 45:40:15 mixture of *trans*-**4c**, **5c**, and *cis*-**4c**. Proton-proton connectivities in this mixture were derived from a COSY experiment,[8] and ^1H-^{13}C one-bond connectivities from an HMQC experiment.[9] The structures of *trans*- and *cis*-**4c** are assigned by analogy with the production of **4e** and **4d**, and also by the similarity of their ^1H NMR data to those reported.[7b] The third product has a single CHBr proton, no alkene ^{13}C NMR resonances, and lacks symmetry, but the chemical shifts are not those of 2-bromocyclohexan-

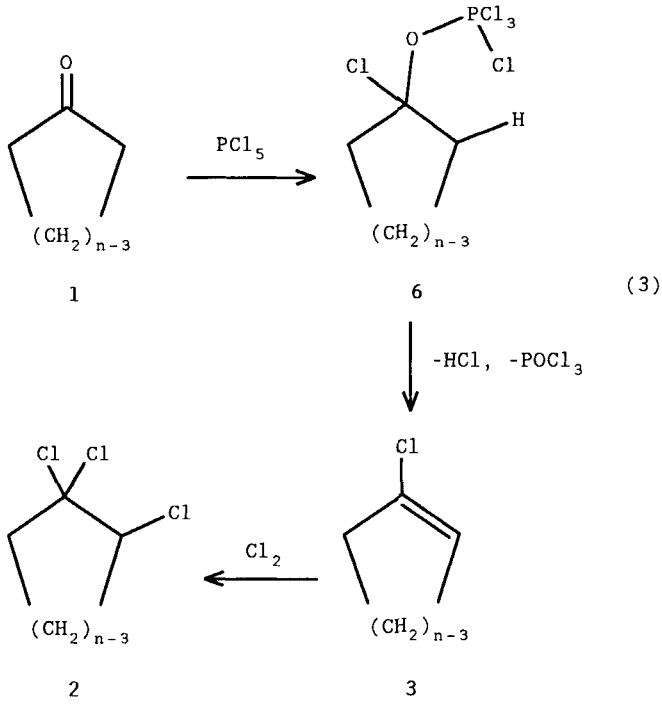
one.[10,11] It is assigned as the previously unknown **5c**; of particular note is the ^{13}C signal at 65.66 ppm bearing no protons, as expected for C(2) of **5c**. Also, the couplings in the CHBr signal of **5c** (dd, J = 12.9, 6.1 Hz) are very like those of *cis*-**4c** (dd, J = 12.3, 5.8 Hz) but unlike those of *trans*-**4c** (dd, J = 7.9, 4.9 Hz): *cis*-**4c** and **5c** should both be conformationally well-defined, with one chair form much more populated than the other, while *trans*-**4c** will be mobile because one bromine must be axial and the other equatorial.

Cyclopentanone (**1b**) reacted with PBr_5 very rapidly and at low temperature (entry 12), to give a mixture of at least three ketones (^{13}C NMR shifts: 211.15, 204.41, 203.29) which decomposed rapidly at room temperature. We could not purify or characterize these species; we speculate that they are α-brominated cyclopentanones or decomposition products therefrom.

Cyclohexanone (**1c**) reacted with PBr_5 (entry 11) much faster than with PCl_5 (entries 3 and 7), and **1b** reacted with PBr_5 even faster than **1c** did (entry 12). Treatment of **1c-e** with phosphorus *tri*bromide (PBr_3) returned the starting ketones.

The rates of our conversions of ketones **1** to trichlorides **2** depend on ring size in essentially the same way as the reported conditions for conversion of **1** to chloroalkenes **3**: essentially no dependence for four to

seven carbons (**1a-d**),[12] but slower for eight (**1e**).[5] Our results are consistent with Newman's mechanistic framework (eq 3) for the conversions of **1** to **3**,[13] wherein



(3)

each chloroalkene forms by loss of HCl and $POCl_3$ from the adduct **(6)** of the ketone and PCl_5. The formation of trichlorides leads us to invoke one more process. Phosphorus pentachloride is known to dissociate thermally into PCl_3 and Cl_2,[14] and has been used as an *in situ* source of Cl_2;[15] we suggest that on prolonged reaction in boiling CCl_4 (~77° C), Cl_2 so generated adds across the C=C bonds of compounds **3** to give trichlorides **2**. The conversion of a **3c/2c** mixture to **2c** (entry 8) ar-

gues in favor of this idea. We did not detect 1,1-dichlorocycloalkanes; any such products must be dehydrochlorinated *in situ*.

The α,α′-brominated ketones produced from **1c-e** and PBr_5 cannot form by processes analogous to those that give compounds **2** and **3**; however, α,α′-dibromoketones are known to form on reaction of **1b-e** with Br_2,[7a,c] and the dissociation of PBr_5 to PBr_3 and Br_2 is much more favorable than that of PCl_5 to PCl_3 and Cl_2.[16] We therefore propose that direct reaction of Br_2 (from PBr_5) with the enol forms of ketones **1c-e** leads to **4c-e** and (by iteration of the sequence) **5c**. Our observation that **1c** and **1b** are brominated faster than **1d** or **1e** is qualitatively consistent with the known higher enol content and enolization rates of **1c** and **1b**.[17]

In sum, we find that PCl_5 and PBr_5 behave differently when cyclic ketones are treated with excess PX_5 in refluxing CCl_4. Under these conditions, PCl_5 acts as a Lewis acid as well as a source of Cl_2, but PBr_5 acts only as a Br_2 source. An isolated example of a similar dichotomy has previously been observed in the reactions of PCl_5 and PBr_5 with dibenzotropone.[18]

The new PCl_5 chemistry should prove useful. It is reported that **2c** is dehydrochlorinated to 1,2-dichlorocyclohexene;[19] we have reproduced this reaction in good yield,[20] and expect it to afford efficient access to other 1,2-dichlorocycloalkenes.

Experimental.

Refractive indices were measured at 25.0 ± 0.5 °C on a Fisher model 5157 refractometer connected to a Polyscience model 910 thermal bath. Infrared (IR) spectra were obtained of neat films on a Perkin-Elmer model 1330 infrared spectrophotometer; Fourier transform IR (FT-IR) spectra were obtained of Nujol mulls on a Nicolet model 550 spectrometer. NMR spectra were obtained of $CDCl_3$ solutions; ^1H spectra were obtained at 360 MHz on a Bruker AMX-360 spectrometer, on which 90-MHz ^{13}C spectra were also run; 50-MHz ^{13}C NMR spectra were obtained on a Varian Gemini 200 spectrometer. Detailed assignments were made with the aid of the DEPT,[21] COSY,[8] and HMQC[9] techniques as specified. Mass spectra were obtained on a Finnigan 3000 spectrometer, by personnel of the Auburn Mass Spectrometry Center. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

General Method. 1,1,2-Trichlorocycloheptane (2d; entry 4). To a solution of **1d** (1.00 g, 1.05 mL, 8.92 mmol) in CCl_4 (40.0 mL) at room temperature was added PCl_5 (6.30 g, 30.3 mmol); the mixture was stirred at reflux under a $CaSO_4$ tube for 24 h, then cooled to room temperature and washed with ice/water (50 mL). The CCl_4 phase was washed with 10% aqueous NaOH until the aqueous phases were no longer colored (5 x 20 mL), and then

with saturated brine (20 mL). Drying ($MgSO_4$), removal of solvent *in vacuo*, and Kugelrohr distillation (aspirator, 120-140°) gave **2d** as a colorless oil (1.18 g, 5.86 mmol, 66%), n_D^{25} 1.5136. IR 2940, 2870, 1455, 1445, 1435, 785, 765, 718. ^1H NMR 4.44 (dd, J = 8.4, 1.8, 1H), 2.72 (ddd, J = 15.1, 9.2, 2.5, 1H), 2.55 ("dd", J = 15.5, 7.5, 1H), 2.32 (dddd, J = 15.2, 8.9, 3.5, 2.5, 1H), 2.04 (dddd, J = 15.7, 8.0, 8.0, 3.3, 1H), 1.90 (ddd, J = 17.9, 8.2, 4.0, 1H), 1.86-1.66 (m, 4H), 1.66-1.52 (m, 1H). ^{13}C NMR (90 MHz, DEPT) 95.97, 72.23, 45.56, 32.49, 25.13, 22.94, 22.26. MS (EI) m/e (%) 202 (0.5), 200 (1.0), 198 (0.4), 167 (10), 166 (10), 165 (16), 164 (15), 131 (35), 130 (15), 129 (100), 128 (11). Anal. (%): C, 41.74; H, 5.54 (calc. for $C_7H_{11}Cl_3$: C, 41.72; H, 5.50).

Other new products:

1,1,2-Trichlorocyclobutane (2a; entry 1). By the General Method, **1a** (0.53 mL, 0.50 g, 7.1 mmol) and PCl_5 (4.5 g, 22 mmol) in CCl_4 (20 mL) at reflux for 72 h gave **2a** as a colorless oil (848 mg, 5.33 mmol, 75%), $bp_{0.1}$ ~20-30, n_D^{25} 1.4866. IR 3020, 2970, 1445, 1435, 785, 770, 725. ^1H NMR 4.68 (dddd, J = 9.2, 8.8, 0.9, 0.5, 1H), 2.92 (dddd, J = 12.6, 9.7, 2.9, 0.9, 1H), 2.75 (dddd, J = 12.6, 10.2, 8.6, 0.5, 1H), 2.57 (dddd, J = 11.2, 8.4, 8.4, 2.8, 1H), 2.29 (dddd, J = 11.0,

9.8, 9.8, 9.8, 1H). ^{13}C NMR (90 MHz, DEPT) 86.01, 64.11, 41.92, 28.44. MS (EI) m/e (%) 160 (2.5), 158 (8.6), 156 (8.4), 125 (10), 124 (2.5), 123 (67), 122 (5.1), 121 (100), 87 (13), 85 (42). Anal. (%) C, 30.26; H, 2.82 (calc. for $C_4H_5Cl_3$: C, 30.13; H, 3.16).

1,1,2-Trichlorocyclooctane (2e; entry 6). By the General Method, **3e** (0.83 g, 5.7 mmol) and PCl_5 (3.9 g, 19 mmol) in CCl_4 (25 mL) at reflux for 5 d gave **2e** as a colorless oil (0.92 g, 4.3 mmol, 75%). IR 2940, 2860, 1450, 790, 765. ^1H NMR 4.56 (dd, J = 7.3, 3.8, 1H), 2.79 (ddd, J = 15.8, 7.6, 3.1, 1H), 2.63 (ddd, J = 15.8, 9.0, 3.0, 1H), 2.20 (m, 2H), 1.78 (m, 2H), 1.69 (m, 2H), 1.61 (m, 4H). ^{13}C NMR (50 MHz) 97.30, 68.89, 44.75, 35.35, 27.11, 26.68, 24.32, 23.27. MS (EI) m/e (%) 216 (1.2), 214 (3.5), 212 (3.6), 181 (3.5), 180 (17), 179 (8.0), 178 (29), 145 (24), 144 (8.4), 143 (75), 67 (100).

Known products:

The following known products had physical and spectroscopic properties consistent with published data and the assigned structures, as specified.

1,1,2-Trichlorocyclopentane (2b; entry 2). By the General Procedure, **1b** (9.5 mL, 9.0 g, 0.12 mol) and PCl_5 (74 g, 0.36 mol) in CCl_4 (0.50 L) at reflux for 72 h gave **2b** after Kugelrohr distillation (aspirator,

80-110°; lit.[5b] bp_{20} 85-87°) as a colorless oil (13.7 g, 79 mmol, 74%), n_D^{25} 1.4964 (lit.[5b] n_D^{25} 1.4920). IR 3000, 2970, 2890, 1470, 1445, 1315, 1170, 1060, 980, 970, 910, 900, 840, 755.[22] ^{1}H NMR 4.40 (dd, J = 6.6, 6.6, 1H), 2.75 (ddd, J = 14.4, 9.4, 5.0, 1H), 2.47 (m, 2H), 2.07 (m, 2H), 1.89 (dddd, J = 14.9, 13.0, 5.0, 5.0, 1H).[23] ^{13}C NMR (90 MHz, DEPT) 93.20, 69.40, 43.79, 31.91, 19.30. Anal. (%) C, 34.51; H, 3.98 (calc. for $C_5H_7Cl_3$: C, 34.62; H, 4.07).

1,1,2-Trichlorocyclohexane (2c; entry 3). By the General Procedure, **1c** (1.00 mL, 0.947 g, 9.66 mmol) and PCl_5 (6.2 g, 30 mmol) in CCl_4 (40 mL) at reflux for 24 h gave **2c** after Kugelrohr distillation (aspirator, 90-110°; lit.[5c] bp_{20} 106-107°) as a clear, colorless oil (1.214 g, 6.48 mmol, 66.4%), n_D^{25} 1.5060 (lit.[5b] n_D^{25} 1.5065). IR 2960, 2870, 1445, 1335, 1250, 1235, 1110, 990, 920, 910, 890, 845, 830, 750. ^{1}H NMR 4.24 (dd, J = 9.6, 3.9, 1H), 2.72 (dddd, J = 14.0, 4.2, 4.2, 0.9, 1H), 2.29-2.17 (m, 2H), 1.99 (dddd, J = 13.8, 10.0, 10.0, 3.8, 1H), 1.85-1.70 (m, 3H), 1.44 (dddd, J = 13.7, 13.7, 9.8, 4.7, 1H).[23] ^{13}C NMR (90 MHz, DEPT) 92.47, 68.46, 44.78, 23.32, 23.21, 22.90. Anal. (%) C, 38.43; H, 4.59 (calc. for $C_6H_9Cl_3$: C, 38.44; H, 4.84).

1-Chlorocyclooctene (3e; entry 5). Colorless oil, n_D^{20} 1.4927 (lit.[24] 1.4928), n_D^{25} 1.4906. IR 3052, 2927, 2855, 2684, 1664, 1466, 1446, 1368, 1224, 1124,

1006, 894, 841, 742, 657.[25] ^{1}H NMR 5.76 (t, J = 8.6, 1H), 2.48 (m, 2H), 2.11 (m, 2H), 1.65 (m, 4H), 1.51 (m, 4H). ^{13}C NMR (90 MHz) 133.93, 121.07, 33.28, 30.09, 27.50, 27.42, 26.37, 25.66.

trans-**2,8-Dibromocyclooctanone (4e; entry 9).** The crude product was ~95% *trans* by ^{1}H NMR. A sample of the *trans* isomer, free (^{1}H NMR) of *cis* isomer, was obtained by two crystallizations from methanol: mp 75.5-76.5 (lit.[6] 75.5-77.5, lit.[7a] 82). FT-IR 1740. ^{1}H NMR 4.64 (dd, J = 11.9, 4.5, 2H), 2.29 (m, 4H), 1.74 (m, 2H), 1.56 (m, 2H), 1.40 (m, 2H).[6] ^{13}C NMR (90 MHz) 202.53, 47.98, 35.55, 25.30, 22.83.

trans-**2,7-Dibromocycloheptanone (4d; entry 10).** The crude product was ~97% *trans* (^{1}H NMR); crystallization from methanol gave a sample of similar composition, mp 61.5-63.5 (lit.[7c] for *trans* isomer, 70-71). FT-IR 1720.[7c,26] ^{1}H NMR 4.72 (dd, J = 10.3, 4.7, 2H), 2.50 (m, 2H), 2.94 (m, 4H), 1.43 (m, 2H).[7c] ^{13}C NMR (90 MHz) 198.52, 49.70, 35.02, 27.04.[7c]

Reaction of 1c with PBr_5:

cis- and *trans*-**2,6-Dibromocyclohexanone** (*cis*- and *trans*-**4c**) and **2,2,6-Tribromocyclohexanone (5c; entry 11).** To a solution of **1c** (0.49 g, 5.0 mmol) in CCl_4 (22.0 mL) at room temperature was added PBr_5 (7.10 g, 16.5 mmol); the orange solution was stirred at reflux

for 125 min. The mixture was cooled to room temperature, poured into ice/water (150 g), and extracted into CH_2Cl_2 (30 mL). The CH_2Cl_2 extract was washed with water (5 x 50 mL), then with brine (4 x 50 mL); drying ($MgSO_4$) and removal of solvent *in vacuo* gave a 45:40:15 mol/mol/mol mixture of *trans*-**4c**, **5c**, and *cis*-**4c** (1.01 g, ~70% yield) as a yellow flowing oil. FT-IR: 2954, 2861, 1762, 1749.[7a,b] *trans*-**4c**: ^{1}H NMR (COSY) 5.03 (dd, J = 7.9, 4.9, 2H), 2.45 (m, 2H), 2.23 (m, 2H), 2.04 (tt, J = 5.8, 5.8, 2H).[7b] ^{13}C NMR (90 MHz, HMQC) 187.89,[27] 50.80, 37.06, 21.60. *cis*-**4c**: ^{1}H NMR (COSY) 4.69 (dd, J = 12.3, 5.8, 2H), 2.70 (m, 2H), 2.17 (m, 2H), 1.84 (m, 2H).[7b] ^{13}C NMR (90 MHz, HMQC) 193.03, 52.63, 38.93, 25.99. **5c**: ^{1}H NMR (COSY) 5.54 (dd, J = 12.9, 6.1, 1H), 3.05 (ddddd, J = 15.2, 2.9, 2.9, 2.9, 0, 1H), 2.70 (m, 2H), 2.17 (m, 3H). ^{13}C NMR (90 MHz, HMQC) 195.43),[27] 65.66, 49.70, 48.62, 38.56, 24.76.

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(27) The C-1 assignments of *trans*-**4c** and **5c** may be reversed.

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