Chlorine *versus* bromine: facial selectivity in the Diels–Alder reactions of 5-bromo-1,2,3,4,5-pentachlorocyclopenta-1,3-diene

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Diels–Alder reactions of diene **11** with both electron-poor and electron-rich dienophiles led to approximately 90% addition to the face of **11** syn to the C-5 chlorine. Addition of 4-phenyl-1,2,4-triazoline-3,5-dione was slightly less facially selective. Adduct ratios were obtained by NMR methods; stereochemistry was determined by X-ray crystallography. The results support the view that facial selectivity in Diels–Alder reactions with heteroatom-substituted dienes is mainly controlled by steric, not stereoelectronic, interactions.

Introduction

Facial selectivity in the Diels–Alder reactions with planenonsymmetric cyclopentadienes substituted at C-5 by a halogen has been examined a number of times. Additions to 1 occurred overwhelmingly syn[‡] to fluorine.¹ Dienes 2–5, with a C-5



chlorine, all favoured syn ‡ addition.²⁻⁵ Bromine and, especially, iodine at C-5, as in 6-9, directed an incoming dienophile anti.4,5 Facial selectivity data had also been reported for two dienes in which chlorine was pitted against a different heteroatom. Reactions of diene 10 were examined rigorously with a variety of dienophiles, and addition was shown to be anti to the C-5 chlorine with every dienophile.⁶ Diene 11 presented a facial choice between chlorine and bromine. Williamson and Hsu³ stated that 11 was too thermally labile to allow a reasonable assessment of its facial selectivity. On the other hand, Shestakova et al.⁷ did report Diels-Alder reactions with 11, but their assignment of the stereochemistry for the adducts was based on an interpretation of the ¹H NMR chemical shift (60 MHz) data that was found to be untenable in the study of 10.6 We chose to re-examine the reactions of 11 with a variety of dienophiles not only because of uncertainty with regard to the published structures of the adducts but more importantly because the results might shed light on how facial selectivity is governed.

Results and discussion

Diene 11 was prepared in good yield by treatment with *N*-bromosuccinimide of the cyclopentadienyl anion derived from

3. Conditions for the Diels-Alder reactions of 11 and the facial selectivities are summarized in Table 1. Electron-deficient dienophiles such as N-phenylmaleimide and 1,4-naphthoquinone were very slow to react, whereas vinylene carbonate, which is electron-rich, reacted more quickly, although its adducts decomposed at elevated temperatures. Every Diels-Alder reaction provided only two adducts, and the NMR data indicated that both adducts were symmetrical. Hence, adducts were not derived from thermally isomerized dienes, and the similarity of chemical shifts suggested that adducts were epimeric at the methano bridge, i.e., not mixtures of endo- and exo-addition products. Integration of the NMR spectra of every product mixture revealed that the ratio of the adducts was very similar (Table 1). The exception was a somewhat lower ratio with 4phenyl-1,2,4-triazoline-3,5-dione (PTAD). We had found, both experimentally⁵ and computationally,⁸ that this dienophile can impart a destabilizing interaction with a syn halogen, similar to the closed-shell repulsion noted by Coxon et al.9 with another diene system.

Column chromatography failed to separate the adducts. Enrichment of any adduct by crystallization was unsuccessful.§ Therefore, the stereochemistry of the adducts from five of the six Diels-Alder reactions was determined by X-ray crystallography with the crystalline mixtures of the syn-anti adduct pairs. In order to effect a structural analysis, each mixture was modelled with both halogens on the methano bridge as bromine, and the proportions of the bromines were varied to obtain the best refinement values. Thus, the bromine occupancy on the methano bridge reflected the proportion of chlorine and bromine on the methano bridge, and the molecular diagrams, e.g. Fig. 1, showed no obvious distortions. Structures 12, 14, 16, 20 and 22 were assigned from the crystallographic work, and spectroscopic parallels allowed a confident assignment of 18 as the major isomer with 3-nitrostyrene. The preferred mode of attack by the dienophile was syn to the chlorine of 11 in every instance. Furthermore, from the optimized partial occupancy data, the proportions of the minor adducts 13, 15, 17 and 23 in the recrystallized samples could be estimated. The adduct mixture derived from vinylene carbonate contained a significant proportion of a third hexachloro component, making estimation of the amount of 21 difficult. Adduct ratios determined in this crystallographic manner should be considered

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[‡] In this paper "*syn*" and "*anti*" are relative to the chlorine at C-5 of the diene, or, for dienes without chlorine at C-5, "*syn*" and "*anti*" are with respect to the heteroatom at C-5.

[§] The adduct mixture derived from vinylene carbonate also cocrystallized with some adduct derived from hexachlorocyclopentadiene.

Table 1 Reaction conditions, yields and facial selectivities of the Diels-Alder reactions of diene 11

Dienophile and reaction conditions	Yield (%)	Adduct ratio by NMR	Adduct ratio by X-ray
<i>N</i> -Phenylmaleimide (2 equiv.); toluene reflux, 21 days 1,4-Naphthoquinone (2 equiv.); toluene reflux, 28 days Styrene (1.5 equiv.); benzene reflux, 6 days 3-Nitrostyrene (1.5 equiv.); toluene reflux, 3 days Vinylene carbonate (1.2 equiv.); neat, 150 °C, 3 h	44 45 63 36 9	12 :13 92:8 14 :15 89:11 16 :17 94:6 18 :19 94:6 20 :21 88:12	12:13 90:10 14:15 95:5 16:17 95:5 20:21 93:7
4-Phenyl-1,2,4-triazoline-3,5-dione (1 equiv.); benzene reflux, 2 days	83	22:23 82:18	22 : 23 85:15



Fig. 1 ORTEP diagram for 22/23.

approximate, but, as shown in Table 1, these ratios were similar to those obtained by NMR techniques.

Steric hindrance and torsional effects have been used to explain the facial selectivity in the Diels-Alder reactions of some cyclic, plane-nonsymmetric dienes,^{4,8,10} but additions to dienes 1,¹ 2,⁵ 24 and analogues¹¹ and 25⁴ all took place preferentially syn to the C-5 heteroatom. These reactions, and the reactions of some dienes fused to bicyclic systems,¹² led to the formulation of a number of hypotheses concerning factors that govern stereoelectronic control of this facial selectivity. The data in Table 1 indicate that none of these phenomena control facial selectivity with 11. That the adduct ratios (Table 1) were the same with N-phenylmaleimide and 1,4-naphthoquinone ("normal" Diels-Alder reactions) as with vinylene carbonate ("inverse-electron-demand") ruled out control of facial selectivity by a facial bias in the π_{HOMO}^{13} or the nucleophilicity ¹⁴ of the diene, or of orbital mixing between the heteroatom lone pairs and the incoming dienophile.¹⁵ Control of facial selectivity in Diels-Alder reactions by a process similar to that originally hypothesized by Cieplak¹⁶ for carbonyl additions would involve at the transition state σ -donation from the anti substituent at C-5 of the diene.^{4,17} σ -Donation by a C–Cl bond should be similar to that of a C–Br bond,¹⁸ so this hypothesis would predict little facial preference with **11**. Williamson and Hsu³ have proposed that van der Waals/London type forces control facial selectivity with 3, and he predicted that, since the polarizability of bromine is greater than that of chlorine, Diels-Alder additions to 11 should be mainly syn to bromine. Photoelectron spectra and calculations by Werstiuk and co-workers¹⁹ have ruled out some of these hypotheses, and a recent *ab initio* computational study pointed out that steric control of facial selectivity with 5-substituted cyclopentadienes correlated very well with a computed steric factor.⁸ That the facial selectivity with diene 11 is little affected by the electronic nature of its Diels-Alder





12 X = Br, Y = C**13** X = CI, Y = BI

16 17 18







reactions is strong experimental corroboration for the proposal for control of facial selectivity by steric effects.

Experimental

General

Uncorrected mps were determined on a Fisher-Johns apparatus. IR spectra were measured as thin films on a Mattson Polaris FT instrument. A General Electric GE 300-NB spectrometer provided the ¹H and ¹³C NMR spectra. Mass spectra (EI) were obtained on a V. G. Micromass 7070HS instrument or a Hewlett-Packard 5970 mass selective detector (GC-MS). The X-ray diffractometer was a Rigaku AFC6S instrument.

5-Bromo-1,2,3,4,5-pentachlorocyclopenta-1,3-diene 11

A 2.5 M solution of n-butyllithium (1.72 ml, 4.31 mmol) in hexane was added dropwise to a solution of 1,2,3,4,5pentachlorocyclopenta-1,3-diene⁵ (0.790 g, 3.32 mmol) in dry tetrahydrofuran (THF) (30 ml) at -78 °C. A solution of Nbromosuccinimide (0.804 g, 4.51 mmol) in THF (15 ml) was added, and the mixture was allowed to warm slowly to room temperature. The solution was concentrated under vacuum, and the orange-brown residue was redissolved in diethyl ether. The solution was washed with H₂O and brine, and dried over anhydrous MgSO₄. Flash chromatography with hexane as the eluent gave *diene* **11** (0.834 g, 79%) as an orange–brown oil: $v_{max}(film)/cm^{-1}1599, 1567, 1231, 1188 and 1136; <math>\delta_{C}$ 133.8, 127.3 and 67.7; *m*/*z* 322 (1%), 320 (5), 318 (9), 316 (10) and 314 (4) all M⁺, 285 (3), 283 (8), 281 (10), 279 (4), 243 (3), 241 (21), 239 (68), 237 (100), 235 (61), 171 (0.2), 169 (5), 167 (15), 165 (16), 134 (3), 132 (14), 130 (23), 97 (10), 95 (31) and 60 (20).

General procedure for the Diels–Alder reactions: ($3a\alpha,4\beta,7\beta,7a\alpha,8s$)- 12 and ($3a\alpha,4\beta,7\beta,7a\alpha,8r$)-8-bromo-4,5,6,7,8-pentachloro-3a,4,7,7a-tetrahydro-2-phenyl-4,7methano-1*H*-isoindole-1,3-(2*H*)-dione 13

A solution of diene 11 (122 mg, 0.385 mmol) and Nphenylmaleimide (125 mg, 0.724 mmol) in toluene (8.0 ml) was heated under reflux for 21 days. The solution was concentrated under vacuum. TLC (EtOAc-hexanes) showed a single spot, but ¹H NMR analysis indicated this was a mixture of **12** and **13**, in a ratio of 11:1, respectively, and unreacted dienophile. The mixture was redissolved in CH2Cl2 (20 ml) and heated under reflux. 1,2,3,4-Tetramethyl-5,5-dimethoxycyclopenta-1,3-diene was added to consume the unreacted dienophile. Flash chromatography (5% EtOAc-hexanes) provided 83 mg (44%) of colourless crystals composed of both 12 and 13, in the same ratio (by ¹H NMR) as before chromatography. Recrystallization (acetone-hexane) gave colourless needles with no change in the 12:13 ratio. For these crystals (Found C, 36.75; H, 1.52; N, 2.83. C₁₅H₇BrCl₅NO₂ requires C, 36.74; H, 1.44; N, 2.86%); mp 235–236 °C; $v_{max}(film)/cm^{-1}$ 1723; δ_{H} (for 12 from mixture) 7.50–7.38 (3 H, m), 7.16–7.09 (2 H, m) and 4.02 (2 H, s); $\delta_{\rm H}$ (for **13** from mixture) 4.08 (s); $\delta_{\rm C}$ (for **12** from mixture) 169.1, 132.1, 130.6, 129.5, 126.4, 95.2, 79.9 and 51.4; $\delta_{\rm C}$ (for 13 from mixture) 94.6; m/z 497 (1%), 495 (6), 493 (21), 489 (38) and 487 (15) all M⁺, 458 (2), 456 (4), 454 (4), 452 (2), 313 (2), 311 (11), 309 (29), 307 (35), 305 (15), 267 (4), 265 (12), 263 (18), 261 (12), 241 (2), 239 (7), 237 (11), 235 (7), 173 (100), 119 (19), 91 (15) and 54 (17).

$(1\alpha,4\alpha,4a\beta,9a\beta,11r)$ - 14 and $(1\alpha,4\alpha,4a\beta,9a\beta,11s)$ -11-bromo-1,2,3,4,11-pentachloro-1,4,4a,9a-tetrahydro-1,4-methanoanthracene-9,10-dione 15

Colourless crystals (mixture of **14** and **15**) were obtained from ether–petroleum ether: mp 139–140 °C; $\delta_{\rm H}$ (for **14** from mixture) 8.02 (2 H, symmetrical m), 7.80 (2 H, symmetrical m) and 4.09 (2 H, s); $\delta_{\rm H}$ (for **15** from mixture) 4.16 (s); $\delta_{\rm C}$ (for **14** from mixture) 189.1, 135.2, 134.7, 132.3, 93.6, 82.3 and 54.2; *mlz* 480 (1%), 479 (0.8), 478 (4), 477 (2), 476 (8), 475 (2), 474 (8), 473 (0.7) and 472 (3) all M⁺, 445 (0.2), 444 (0.1), 443 (2), 442 (1), 441 (4), 440 (1), 439 (5), 438 (0.7), 437 (3), 435 (0.2), 402 (0.5), 401 (1), 400 (0.5), 399 (3), 398 (2), 397 (8), 396 (2), 395 (12), 394 (2), 393 (7), 366 (0.4), 355 (1), 364 (2), 363 (2), 362 (6), 361 (4), 360 (14), 359 (6), 358 (13), 357 (4), 356 (3), 326 (3), 325 (9), 324 (6), 323 (10), 322 (12), 321 (3), 320 (43), 319 (5), 318 (83), 317 (5), 316 (81), 315 (2), 314 (33), 245 (0.7), 238 (9), 237 (100), 236 (6), 235 (61), 169 (22), 167 (64), 158 (12), 104 (66), 76 (98) and 50 (41).

(1*R**,4*S**,5*R**,7*R**)- 16 and (1*R**,4*S**,5*R**,7*S**)-7-bromo-1,2,3,4,7-pentachloro-5-phenylbicyclo[2.2.1]hept-2-ene 17

Colourless crystals (mixture of **16** and **17**) were obtained from ether–petroleum ether (Found C, 37.08; H, 1.73. $C_{13}H_8BrCl_5$ requires C, 37.06; H, 1.91%); mp 67–68 °C; $v_{max}(film)/cm^{-1}$ 1603; δ_H (for **16** from mixture) 7.33 (3 H, narrow m), 7.10 (2 H, narrow m), 4.01 (1 H, dd, *J* 4.3 and 9.1), 2.96 (1H, dd, *J* 9.1 and 12.9) and 2.51 (1H, dd, *J* 4.3 and 12.9); δ_H (for **17** from mixture) 134.3, 132.3, 132.2, 128.9, 128.5, 94.6, 84.5, 79.4, 51.1 and 39.9; δ_C (for **17** from mixture) 52.1 and 41.1; *m/z* 424 (0.5%), 420 (0.5) and 418 (0.1) all M⁺, 243 (0.2), 241 (1), 239 (3), 238 (0.7), 237 (5), 236 (0.5), 235 (4), 234 (0.8), 233 (3), 127 (16), 125 (55), 104 (100), 103 (10), 78 (11), 77 (7) and 51 (6).

(1*R**,4*S**,5*R**,7*R**)- 18 and (1*R**,4*S**,5*R**,7*S**)-7-bromo-1,2,3,4,7-pentachloro-5-(3-nitrophenyl)bicyclo[2.2.1]hept-2-ene 19

Colourless crystals (mixture of 18 and 19) were obtained from ether-ethyl acetate-petroleum ether: mp 116-117 °C; v_{max}(film)/ cm⁻¹ 1601, 1530 and 1349; $\delta_{\rm H}$ (for **18** from mixture) 8.22 (1 H, d, J 8.1), 8.02 (1 H, narrow m), 7.58-7.43 (2 H, m), 4.14 (1 H, dd, J 4.3 and 9.2), 3.05 (1 H, dd, J 9.2 and 12.8) and 2.54 (1 H, dd, J 4.3 and 12.8); $\delta_{\rm H}$ (for 19 from mixture) 4.20 (1 H, dd, J 4.8 and 9.8); $\delta_{\rm C}$ (for **18** from mixture) 148.2, 136.7, 134.7, 133.2, 131.6, 129.6, 123.9, 123.5, 93.9, 84.3, 79.2, 50.8 and 39.9; $\delta_{\rm C}$ (for 19 from mixture) 51.8 and 41.1; m/z 471 (0.6%), 470 (0.2), 469 (2), 468 (0.5), 467 (3), 466 (0.6), 465 (3), 464 (0.1) and 463 (1) all M⁺, 324 (2), 323 (1), 322 (14), 321 (3), 320 (50), 319 (6), 318 (99), 317 (6), 316 (100), 315 (2), 314 (38), 310 (2), 300 (0.8), 299 (10), 298 (2), 297 (25), 296 (2), 295 (31), 294 (1), 293 (14), 243 (3), 242 (1), 241 (19), 240 (3), 239 (57), 238 (5), 237 (88), 236 (3), 235 (55), 220 (2), 219 (0.7), 218 (5), 217 (1), 216 (11), 215 (1), 214 (9), 172 (9), 170 (28), 149 (15), 133 (14), 103 (33) and 77 (34).

(3aα,4β,7β,7aα,8s)- 20 and (3aα,4β,7β,7aα,8r)-8-bromo-4,5,6,7,8-pentachloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one 21

Sublimation then recrystallization from ether–petroleum ether gave colourless crystals (mixture of **20**, **21** and the adduct derived from hexachlorocyclopentadiene): mp 145–155 °C (subl.); $v_{max}(film)/cm^{-1}$ 1822; δ_{H} (for **20** from mixture) 5.40 (s); δ_{H} (for **21** from mixture) 5.44 (s); δ_{H} (for hexachloro adduct from mixture) 5.37 (s); δ_{C} (for **20** from mixture) 151.3, 132.7, 88.8, 82.0 and 81.1; *m/z* (GC–MS) 406 (3%), 404 (14) and 402 (11) all M⁺, 322 (18), 320 (59), 319 (17), 318 (98), 317 (2), 316 (100), 314 (38), 296 (15), 294 (18), 292 (9), 254 (2), 252 (16), 251 (7), 250 (23), 249 (2), 248 (16), 241 (17), 239 (59), 238 (3), 237 (86), 236 (2), 235 (55), 218 (17), 217 (10), 216 (40), 215 (21), 214 (34), 213 (16), 145 (17), 144 (10), 143 (33), 142 (4), 141 (15), 108 (40) and 73 (19).

(10s)- 22 and (10r)-10-bromo-5,6,7,8,10-pentachloro-5,8dihydro-2-phenyl-5,8-methano-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione 23

Colourless crystals (mixture of **22** and **23**) were obtained from CH₂Cl₂–hexane (Found C, 31.69; H, 1.00; N, 8.50. C₁₃H₅BrCl₅-N₃O₂ requires C, 31.71; H, 1.02; N, 8.53%); mp 137–141 °C but turning pink first at 130 °C; v_{max} (film)/cm⁻¹ 3076, 3046, 3022, 1804, 1749 and 1596; $\delta_{\rm C}$ (for **22** from mixture) 154.6, 129.6, 129.5, 129.4, 125.5, 92.7 and 87.0; $\delta_{\rm C}$ (for **23** from mixture) 127.8 and 86.4; *m*/*z* 460 (0.4%), 458 (1.5), 456 (1.7) and 454 (0.7) all M⁺ – Cl, 324 (0.6), 322 (5), 320 (18), 318 (34), 316 (34), 314 (13), 287 (0.3), 285 (3), 283 (7), 281 (8), 279 (4), 243 (3), 241 (20), 239 (64), 237 (100), 235 (62), 119 (68), 91 (31) and 64 (19).

X-Ray analysis of 12/13

Crystal data. Colourless irregular crystal $0.15 \times 0.10 \times 0.40$ mm; C₁₅H₇BrCl₅NO₂, M = 490.39. Monoclinic, a = 7.762(2), b = 37.419(2), c = 12.518(2) $\beta = 90.81(2)^{\circ}$, V = 3635.4(8) Å³ (from a least-squares refinement using the settings of 16 carefully centred reflections in the range $58.52 < 2\theta < 59.69^{\circ}$, $\lambda = 1.54178$ Å, T = 26.0 °C), space group $P2_1/c$ (#14), Z = 8, $D_{calc} = 1.79$ g cm⁻³, μ (Cu-K α) = 99.3 cm⁻¹.

Data collection and processing. Graphite-monochromated Cu-K α radiation, ω -2 θ scans, with 2 θ maximum 120.1°, ω scan width $(0.94 + 0.14 \tan \theta)^\circ$; 5985 reflections collected $(2.5 \le \theta \le 60^\circ, \pm 8 h, \pm 40 k, 14 l)$, of which 5533 ($R_{int} = 0.034$) were unique. Intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. An empirical absorption correction based on

azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.68 to 1.00. Data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = $6.41292e^{-7}$).

Structure analysis and refinement. The structure was solved by and expanded using Fourier techniques.²⁰ Non-H atoms were refined anisotropically; H atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3340 observed reflections $(I = 2.00\sigma(I))$ and 434 variable parameters and converged (largest parameter shift was 0.00 times its esd). With 90% bromine anti at C-8, the agreement factors were $R (\Sigma(|F_o| - |F_c|)/\Sigma|F_o|) = 0.045$ and R_w $([\Sigma_{\rm w}(|F_{\rm o}| - |F_{\rm c}|)^2 / \Sigma_{\rm w} F_{\rm o}^2)]^{1/2}) = 0.046$ with GOF = 1.64 (for 85% bromine *anti* at C-8, R = 0.047, $R_w = 0.048$, GOF = 1.71; for 95% bromine anti at C-8, R = 0.047, $R_w = 0.049$, GOF = 1.76). The weighting scheme was based on counting statistics and included a factor (p = 0.022) to downweight the intense reflections. Plots of $\Sigma_{\rm w}(|F_{\rm o}| - |F_{\rm c}|)^2$ versus $|F_{\rm o}|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to +0.44 and -0.45 e Å⁻³, respectively. Neutral atom scattering factors were from the International Tables for X-ray Crystallography.^{21a} Anomalous dispersion effects were included in F_{calc} ;²² the values for $\Delta f'$ and $\Delta f''$ and for the mass attenuation coefficients were from the International Tables for Crystallography.^{23a,b} Calculations used the TEXSAN crystallographic software package.24

X-Ray analysis of 14/15

Crystal data. Colourless irregular crystal $0.20 \times 0.05 \times 0.40$ mm mounted on a glass fibre; $C_{15}H_6BrCl_5O_2$, M = 475.38. Triclinic, a = 13.562(5), b = 14.154(5), c = 11.188(2) Å, a = 108.29(2), $\beta = 95.32(2)$, $\gamma = 116.92(3)^\circ$, V = 1746.8(13) Å³ (from a least-squares refinement using the settings of 21 carefully centred reflections in the range $20.08 < 2\theta < 25.10^\circ$, $\lambda = 0.71069$ Å, T = 26.0 °C), space group *P*-1 (#2), Z = 4, $D_{calc} = 1.81$ g cm⁻³, μ (Mo-K α) = 31.3 cm⁻¹.

Data collection and processing. Graphite-monochromated Mo-K α radiation, $\omega + 2\theta$ scans, with 2θ maximum 50.1°, ω scan width (1.15 + 0.35 tan θ)°; 6459 reflections collected (2.5 $\leq \theta \leq 25^{\circ}$, $\pm 16 h$, $\pm 16 k$, 13 *l*), of which 6174 ($R_{int} = 0.051$) were unique. Intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.74 to 1.00. Data were corrected for Lorentz and polarization effects.

Structure analysis and refinement. The structure was solved by direct methods and expanded Fourier techniques.^{20,25} Non-H atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2811 observed reflections $(I = 2.00\sigma(I))$ and 415 variable parameters and converged (largest parameter shift was 0.00 times its esd). With 95% bromine anti at C-11, the agreement factors were R = 0.049 and $R_{\rm w} = 0.047$ with GOF = 1.41 (for 90% bromine *anti* at C-11, $R = 0.050, R_w = 0.047, \text{GOF} = 1.44; \text{ for } 100\% \text{ bromine anti at C-}$ 11, R = 0.051, $R_w = 0.050$, GOF = 1.52). The weighting scheme was based on counting statistics and included a factor (p = 0.027) to downweight the intense reflections. Plots of $\Sigma_{\rm w}(|F_{\rm o}| - |F_{\rm c}|)^2$ versus $|F_{\rm o}|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to +0.47 and -0.45 e Å⁻³, respectively. Neutral atom scattering factors were from the International Tables for X-ray Crystallography.^{21a} Anomalous dispersion effects were included in F_{calc} .²² The values for $\Delta f'$ and $\Delta f''$ were from the International Tables for Crystallography.^{23a} Calculations used the TEXSAN crystallographic software package.²⁴

X-Ray analysis of 16/17

Crystal data. Colourless irregular crystal $0.20 \times 0.30 \times 0.40$ mm mounted on a glass fibre; C₁₃H₈BrCl₅, M = 421.38. Monoclinic, a = 14.075(2), b = 10.224(3), c = 11.551(3) Å, $\beta = 70.33(2)^{\circ}$, V = 1565(1) Å³ (from a least-squares refinement using the settings of 14 carefully centred reflections in the range 29.45 < 2θ < 32.39°, $\lambda = 0.71069$ Å, T = 26.0 °C), space group $P2_1/c$ (#14), Z = 4, $D_{calc} = 1.788$ g cm⁻³, μ (Mo-K α) = 34.4 cm⁻¹.

Data collection and processing. Graphite-monochromated Mo-K α radiation, ω -2 θ scans, with 2 θ maximum 50.1°, ω scan width (1.37 + 0.35 tan θ)°; 3083 reflections collected (2.5 $\leq \theta \leq 25^{\circ}$, $\pm 16 h$, $\pm 12 k$, 13 *l*), of which 2941 ($R_{int} = 0.050$) were unique. Intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.87 to 1.00. Data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.33243e⁻⁷).

Structure analysis and refinement. The structure was solved by direct methods.^{20,26} Non-H atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1573 observed reflections ($I < 2.0\sigma(I)$) and 197 variable parameters and converged (largest parameter shift was 0.00 times its esd). With 95% bromine anti at C-7, the factors were R = 0.041 and $R_w = 0.040$ with GOF = 1.40 (for 90% bromine anti at C-7, R = 0.045, $R_w = 0.043$, GOF = 1.52; for 100% bromine *anti* at C-7, R = 0.043, $R_w = 0.043$, GOF = 1.50). The weighting scheme was based on counting statistics and included a factor (p = 0.030) to downweight the intense reflections. Plots of $\Sigma_{\rm w}(|F_{\rm o}| - |F_{\rm c}|)^2$ versus $|F_{\rm o}|$, reflection order in data collection, $\sin \theta / \lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to +0.33 and -0.44 e Å⁻³, respectively. Neutral atom scattering factors and the values for $\Delta f'$ and $\Delta f''$ were from the International Tables for X-ray Crystallography.^{21a,b} Anomalous dispersion effects were included in F_{calc} ²² Calculations used the TEXSAN crystallographic software package.27

X-Ray analysis of 20/21

Crystal data. Colourless irregular crystal $0.30 \times 0.25 \times 0.40$ mm mounted on a glass fibre; $C_8H_2Br_{0.7}Cl_{5.3}O_3$, M = 389.94. Monoclinic, a = 12.453(2), b = 23.838(2), c = 8.853(5) Å, $\beta = 84.84(3)^\circ$, V = 2617(2) Å³ (from a least-squares refinement using the settings of 20 carefully centred reflections in the range $23.85 < 2\theta < 31.07^\circ$, $\lambda = 0.71069$ Å, T = 26.0 °C), space group $P2_1/c$ (#14), Z = 8, $D_{calc} = 1.979$ g cm⁻³, μ (Mo-K α) = 32.8 cm⁻¹.

Data collection and processing. Graphite-monochromated Mo-K α radiation, ω -2 θ scans, with 2 θ maximum 50.1°, ω scan width (1.15 + 0.35 tan θ)°; 5081 reflections collected (2.5 $\leq \theta \leq 25^{\circ}, \pm 14 h, \pm 28 k, 10 l$), of which 4763 ($R_{int} = 0.044$) were unique. Intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.89 to 1.00. Data were corrected for Lorentz and polarization effects.

Structure analysis and refinement. The structure was solved by direct methods.^{20,26} Non-H atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2180 observed reflections ($I < 2.0\sigma(I)$) and 307

variable parameters and converged (largest parameter shift was 0.00 times its esd). With 65% bromine anti at C-8 (20), 5% syn at C-8 (21) and 30% of the hexachloro-adduct, the agreement factors were R = 0.047 and $R_w = 0.047$ with GOF = 1.46 (for 70% **20** and 30% of the hexachloro-adduct R = 0.049, $R_{\rm w} = 0.048$, GOF = 1.51; for 65% **20**, 8% **21** and 27% hexachoro-adduct R = 0.049, $R_w = 0.048$, GOF = 1.51). The weighting scheme was based on counting statistics and included a factor (p = 0.030) to downweight the intense reflections. Plots of $\Sigma_{\rm w}(|F_{\rm o}| - |F_{\rm c}|)^2$ versus $|F_{\rm o}|$, reflection order in data collection, $\sin \theta / \lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to +0.45 and -0.40 e Å⁻³, respectively. Neutral atom scattering factors and the values for $\Delta f'$ and $\Delta f''$ were from the International Tables for X-ray Crystallography.^{21a,b} Anomalous dispersion effects were included in F_{calc}^{22} Calculations used the TEXSAN crystallographic software package.²⁷

X-Ray analysis of 22/23

Crystal data. Colourless irregular crystal $0.30 \times 0.30 \times 0.30$ mm mounted on a glass fibre; $C_{13}H_5BrCl_5N_3O_2$, M = 492.37. Monoclinic, a = 9.019(6), b = 13.339(9), c = 14.876(4) Å, $\beta = 104.00(4)^\circ$, V = 1736.4(15) Å³ (from a least-squares refinement using the settings of 21 carefully centred reflections in the range $36.70 < 2\theta < 44.96^\circ$, $\lambda = 0.71069$ Å, T = 26.0 °C), space group $P2_1/c$ (#14), Z = 4, $D_{calc} = 1.88$ g cm⁻³, μ (Mo-K α) = 31.5 cm⁻¹.

Data collection and processing. Graphite-monochromated Mo-K α radiation, ω -2 θ scans, with 2 θ maximum 50.1°, ω scan width (0.94 + 0.35 tan θ)°; 3435 reflections collected (2.5 $\leq \theta \leq 25^{\circ}$, $\pm 10 h$, $\pm 15 k$, 17 *l*), of which 3222 ($R_{int} = 0.023$) were unique. Intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.92 to 1.00. Data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 1.58686e⁻⁷).

Structure analysis and refinement. The structure was solved by direct methods and expanded Fourier techniques.20,25 Non-H atoms were refined anisotropically. The H-atom coordinates were refined but their isotropic B's were held fixed. The final cycle of full-matrix least-squares refinement was based on 2285 observed reflections ($I < 2.0\sigma(I)$) and 233 variable parameters and converged (largest parameter shift was 0.00 times its esd). With 85% bromine anti at C-10, the agreement factors were R = 0.038 and $R_{w} = 0.038$ with GOF = 1.87 (for 75%) bromine anti at C-10, R = 0.048, $R_w = 0.052$, GOF = 2.58; for 95% bromine *anti* at C-10, R = 0.045, $R_w = 0.050$, GOF = 2.49). The weighting scheme was based on counting statistics and included a factor (p = 0.020) to downweight the intense reflections. Plots of $\Sigma_{\rm w}(|F_{\rm o}| - |F_{\rm c}|)^2$ versus $|F_{\rm o}|$, reflection order in data collection, $\sin \theta / \lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to +0.41 and -0.40 e Å⁻³, respectively. Neutral atom scattering factors were from the International Tables for X-ray Crystallography.^{21a} Anomalous dispersion effects were included in F_{calc}^{22} The values for $\Delta f'$ and $\Delta f''$ and the values for the mass attenuation coefficients were from the International Tables for Crystallography.^{23a,b} Calculations used the TEXSAN crystallographic software package.24

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/265.

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