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# AN UNUSUAL CHLORINATION OF 1-PHENYL-4-(2,6-DICHLOROPHENYL)-1,3-BUTADIENE

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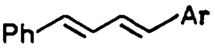
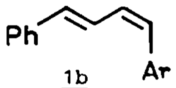
ABSTRACT: The diene 1a reacted with $CHCl_3$/aq. NaOH/PTC in $CH_2Cl_2$ unexpectedly to give a mixture of the chlorination products 2 and 3a. Usual chlorination with $Cl_2$ yielded similarly 2, 3a, and 3b dependent on the amount of $Cl_2$. The formation of 2 as well as the reaction of 7 to give 9 (besides 8) shows an unusual Cl-Cl-interaction.

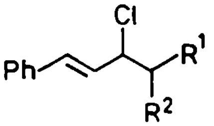
In the precedent paper[1] we mentioned that the reaction of the title compound 1a with a slight excess of $CCl_2$ in methylene chloride did not result in a dichlorocyclopropanation but in a chlorination of the double bonds. This behaviour is quite unusual, particularly with respect to Dehmlows publication[2] about side reactions of dihalocarbene generation via phase transfer catalysts (PTC). He found some radical induced side reactions of very unreactive olefins, but only with bromoform/sodium hydroxide, never with chloroform.

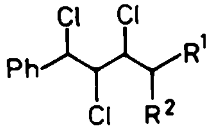


1a

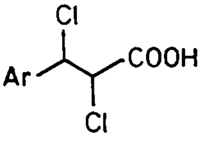


1b

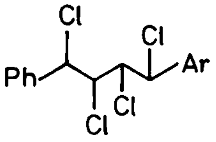




2 $R^1$ = Ar, $R^2$ = Cl 3a
5 $R^1$ = Cl, $R^2$ = Ar 6



4



3b

Ar = 2,6-dichlorophenyl

## Results and Discussion

Reaction of 1a with $CHCl_3$/aq. NaOH/PTC in $CH_2Cl_2$ gave a mixture of the monoadduct 2 and the bisadduct 3a. No trace of a dichlorocyclopropane could be found. The structure of 2 was established by ozonolysis to give benzoic acid, and (2,6-dichlorophenyl)-dichloropropionic acid 4 after oxidative work-up.

The structure of 2 is unexpected, because obviously the more hindered double bond has reacted. The only explanation is a Cl-Cl-interaction. The regioselectivity of this addition must be very strong, because reaction of 1a with molar amounts of $Cl_2$ in $CCl_4$ gave only 2 in high yield. The product derived by addition of chlorine to the other double bond could not be found. Further addition of chlorine to 1a leads to a mixture of 2, 3a and 3b, and after some minutes 1a is completely converted to 3a and 3b. Peculiarly, the isomer 3b is the main product. Assuming trans-addition of chlorine to the olefinic double bonds, two isomers can be formed. There is no evidence for an assignment of the configuration but the melting points. The considerably higher value of 156-159

°C for 3a in comparison to 75-79 °C for 3b might serve as an indication for a quasi-syndiotactic pattern.

The cis,trans-isomer 1b reacts with molar amounts of chlorine similarly as 1a does. Besides a small amount of bisadduct 6, 75% of the monoadduct 5 formed by attack to the cis double bond could be isolated. Again, the isomeric product by reaction with the trans double bond could not be found. In this case, the higher reactivity of the cis double bond might be considered.

The diene 7 finally did not react at all with the $CHCl_3/NaOH/PTC/CH_2Cl_2$ system. With one equivalent of chlorine 1,2- (8) and 1,4-addition product (9) was formed. The occurence of 9 (no analogous products were found with 1a and 1b) shows again the unusual chlorine-chlorine interaction.

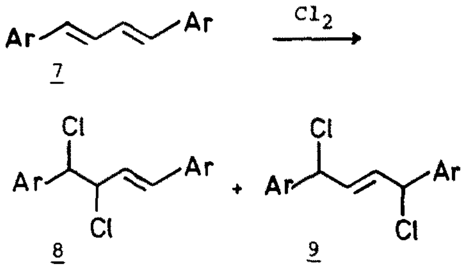


Table 1. Chlorination of 1a; ratio of $Cl_2$-mono- (2) and bis-adducts (3a, b) dependent on reaction conditions

| reaction conditions | isolated yield (%) 2 | 3a | 3b |
|---|---|---|---|
| $CHCl_3/NaOH/PTC$ in $CH_2Cl_2$ | 35 | 23 | -- |
| molar amount $Cl_2$ in $CCl_4$ | 84 | -- | -- |
| $Cl_2$-stream, 4 min | 40 | 45[a] | |
| $Cl_2$-stream, 15 min | -- | 15 | 72 |

[a] isomers not separated

## EXPERIMENTAL

General remarks: see the preceding paper. - Mass spectra: Varian MAT 711.

### Chlorination of (E,E)-1-Phenyl-4-(2,6-dichlorophenyl)-1,3-butadiene (1a)

A) with $CHCl_3$/aq. NaOH/PTC/$CH_2Cl_2$

From 0.40 g (1.5 mmol) 1a according to method A[1] 0.60 g crude product were obtained. A soln in 30 ml petroleum ether was kept 3 d at -5 °C yielding 0.17 g (35%) R*S*-3,4-dichloro-(E)-1-phenyl-4-(2,6-dichlorophenyl)-1-butene (2), m.p. 113-117 °C. $^1$H-NMR: δ 5.76 (dd, J = 10.5; 8.5 Hz, 3-H), 5.92 (d, J = 10.5 Hz, 4-H), 6.34 (dd, J = 16; 8.5 Hz, 2-H), 6.85 (d, J = 16 Hz; 1-H), 7.2-7.5 (m, H-Ph). - $^{13}$C-NMR: δ 59.3 (d, C-3), 61.5 (d, C-4), 126.7-136.6 (olefinic and aromatic C). - MS: m/e = 344, 346, 348 ($M^+$, Cl-isotope pattern, < 1%), 238, 240 (M - 2 Cl, - HCl, 4), 202 (M - 2 Cl, - 2 HCl, 17), 151 (80), 115 (100). The mother liquor was chromatographed with P/E (99.5:0.5) to give 0.15 g viscous oil. Storing in a refrigerator for 4 d, and adding some drops of petroleum ether furnished 0.14 g (23%) crystalline R*,R*,S*,S*(?)-1,2,3,4-tetrachloro-1-phenyl-4-(2,6-dichlorophenyl)-butane (3a), m.p. 156-159 °C. $^1$H-NMR: δ 4.00 (dd, J = 10; 1.5 Hz, 2-H), 4.79 (dd, J = 9.5; 1.5 Hz; 3-H), 5.10 (d, J = 10 Hz, 1-H), 5.92 (d, J = 9.5 Hz, 4-H), 7.25-7.45 (m, H-Ph). - $^{13}$C-NMR: δ 61.7 (d, C-2), 65.0 (d, C-3), 66.1 (d, C-1), 66.8 (d, C-4), 127.9-136.4 (aromatic C). - MS: m/e = 414, 416, 418, 420 ($M^+$, Cl-isotope pattern, 3%), 236, 238 (M - 3 HCl, - 2 Cl, 3), 193, 195, 197 (18), 127(100).

B) with molar amounts of $Cl_2$

15 ml of a 4% soln of $Cl_2$ in $CCl_4$ were dropped to a stirred soln of 2.0 g (7.3 mmol) 1a in 50 ml $CCl_4$ at 0 °C. Stirring at 0 °C was continued for 2 h. After removal of the solvent the crude residue was crystallized from petroleum ether to give 2.1 g (84%) 2.

C) with a $Cl_2$-stream for 4 min

A stream of dry $Cl_2$ was passed through a soln of 0.3 g (1.1 mmol) 1a in 70 ml $CHCl_3$ at 0 °C for 4 min. Then the solvent was removed immediately, and 0.38 g crude product remained. Crystallization from petroleum ether in a refrigerator yielded 0.15 g (40%) 2. Evaporation of the mother liquor gave 0.18 g (45%) of a mixture of 3a and b.

D) with a $Cl_2$-stream for 15 min

Analogously to C). 1.8 g (6.5 mmol) 1a in 170 ml $CHCl_3$ after 15 min yielded 3.3 g crude product, which was chromatographed with P/E (99:1) to give 1.95 g (72%) 3b and 0.40 g (15%) 3a.

### R*,R*,R*,R*(?)-1,2,3,4-Tetrachloro-1-phenyl-4-(2,6-dichlorophenyl)-butane. (3b).

m.p. 75-79 °C. - $^{1}$H-NMR: $\delta$ 4.82 (dd, $J$ = 11; 1.5 Hz, 2-H), 5.10 (d, $J$ = 11 Hz, 1-H), 5.18 (dd, $J$ = 11; 1.5 Hz, 3-H), 6.12 (d, $J$ = 11 Hz, 4-H), 7.1-7.5 (m, H-Ph). - $^{13}$C-NMR: $\delta$ 57.0 (d, C-2), 60.5 (d, C-3), 65.8 (d, C-1), 66.8 (d, C-4), 127.5-137.1 (aromatic C). - MS: m/e = 414, 416, 418, 420 ($M^+$, Cl isotope pattern, 4%), 236, 238 (M - 3 HCl, - 2 Cl, 3), 193, 195, 197 (20), 125 (100).

### Chlorination of (E)-1-Phenyl-(Z)-4-(2,6-dichlorophenyl)-1,3-butadiene (1b).

5 ml of a 4% soln of $Cl_2$ in $CHCl_3$ were added to a stirred soln of 0.65 g (2.4 mmol) 1b in 20 ml $CHCl_3$ at 0 °C. After 1 h at 0 °C the solvent was removed to yield 0.88 g crude product. Addition of petroleum ether to give a clear soln and storing at -5 °C for 3 d yielded 0.08 g (8%) R*,R*,S*,R*(?)-1,2,3,4-tetrachloro-1-phenyl-4-(2,6-dichlorophenyl)-butan (6), m.p. 138-143 °C. - $^{1}$H-NMR: $\delta$ 4.01 (dd, $J$ = 10; 2 Hz, 2-H), 4.78 (dd, $J$ = 9.5; 2 Hz, 3-H), 5.00 (d, $J$ = 10 Hz; 1-H), 5.91 (d, $J$ = 9.5 Hz, 4-H), 7.1-7.45 (m, H-Ph). - MS: m/e = 414, 416, 418, 420 ($M^+$, Cl isotope pattern, 2%), 273, 275, 277 (M - HCl, - 3 Cl, 2), 238, 240 (M - HCl, - 4 Cl, 2), 202 (M - 2 HCl, - 4 Cl, 8), 125 (100).

Concentration of the mother liquor and storing at room temp. for 7 d yielded 0.61 g (75%) R*,R*-3,4-dichloro-(E)-1-phenyl-4-(2,6-dichlorophenyl)-1-butene (5), m.p. 103-107 °C. - $^{1}$H-NMR: $\delta$ 5.74 (dd, $J$ = 11; 9 Hz, 3-H), 5.90 (d, $J$ = 11 Hz, 4-H), 6.33 (dd, $J$ = 16; 9 Hz, 2-H), 6.85 (d, $J$ = 16 Hz, 1-H), 7.2-7.5 (m, H-Ph). - $^{13}$C-NMR: $\delta$ 59.2 (d, C-3), 61.5 (d, C-4), 126.6-136.5 (olefinic and aromatic C). MS: m/e = 344, 346, 348, 350 ($M^+$, Cl isotope pattern, 6%), 309, 311, 313 (M - Cl, 2), 273, 275, 277 (M - HCl, - Cl, 9), 238, 240 (M - HCl, - 2 Cl, 12), 202 (M - 2 HCl, - 2 Cl, 30), 151 (100).

### Chlorination of (E,E)-1,4-Bis-(2,6-dichlorophenyl)-1,3-butadiene (7).

Analogously to 1b. 0.36 g (1.05 mmol) 7 were treated with molar amounts of $Cl_2$ in $CHCl_3$. 0.51 g crude product were chromatographed with P/E (99:1) to give a viscous oil as first fraction. Crystallization from ether at -5 °C yielded 0.14 g 1,4-dichloro-1,4-bis-(2,6-dichlorophenyl)-(E)-2-butene (9), m.p. 165-167 °C. - $^{1}$H-NMR: $\delta$ 6.38, 6.45 (AA'BB'-system, $J_{AB'} = J_{A'B}$ = 1.5 Hz; $J_{AB} = J_{A'B'}$ = 3 Hz; $J_{AA'} = J_{BB'}$ = 0 Hz, 1-,2-,3-,4 4-H), 7.15-7.40 (m, H-Ph). - $^{13}$C-NMR: $\delta$ 56.3 (d, C-1,-4), 129.6-135.5 (olefinic and aromatic C). - MS: m/e = 412, 414, 416, 418 ($M^+$, Cl isotope pattern, 6%), 377, 379, 381, 383 (M - Cl, 30), 341, 343, 345, 347 (M - HCl, - Cl, 20), 306, 308, 310 (M - HCl, - 2 Cl, 24), 270, 272, 274 (M - 2 HCl, - 2 Cl, 30), 236, 238 (M - HCl, - 4 Cl, 50), 219 (100).

A second fraction was obtained as a viscous oil. Crystallization from petroleum ether at -5 °C for 3 d yielded 0.15 g R*,S*-3,4-dichloro-(E)-1,4-bis-(2,6-dichlorophenyl)-1-butene (8), m.p. 130-133 °C. - $^{1}$H-NMR: $\delta$ 5.77 (dd, $J$ = 10; 10 Hz, 3-H), 5.97 (d, $J$ = 10 Hz, 4-H), 5.98 (dd, $J$ = 16; 10 Hz, 2-H), 6.63 (d, $J$ = 16 Hz, 1-H), 7.15-7.35 (m, H-Ph). $^{13}$C-NMR: $\delta$ 61.9 (d, C-3), 64.3 (d, C-4), 127.9-135.7 (olefinic and aromatic C). - MS: m/e = 412, 414, 416, 418 ($M^+$, Cl isotope pattern, 4%), 377, 379, 381, 383 (M - Cl, 35), 341, 343, 345, 347 (M - HCl, - Cl, 20), 306, 308, 310 (M - HCl, - 2 Cl, 24), 270, 272, 274 (M - 2 HCl, - 2 Cl, 25), 236, 238 (M - HCl, - 4 Cl, 50), 219 (100).

### Ozonolysis of 2

0.47 g (1.4 mmol) 2 were ozonolyzed as described previously[1] to give 0.40 g crude product. Chromatography with P/E (1:1), then with pure ether furnished 115 mg (70%) benzoic acid, m.p. 120-122 °C as first fraction (identical with an authentic sample). As second fraction 170 mg (42%) 2,3-dichloro-3-(2,6-dichlorophenyl)-propanoic acid (4) were obtained, m.p. 106-110 °C. - $^{1}$H-NMR: $\delta$ 5.55 (d, $J$ = 10.5 Hz, 2-H), 6.28 (d, $J$ = 10.5 Hz, 3-H), 7.25-7.45 (m, H-Ph), 10.8 (s, COOH). - MS: m/e = 286, 288, 290 ($M^+$, Cl isotope pattern, < 1%), 190, 192, 194 (40), 173, 175, 177 (90), 145 (30), 109 (50), 75 (100).

| Analyses: | | Calculated | | Found | |
|---|---|---|---|---|---|
| | | C | H | C | H |
| 2 | $C_{16}H_{12}Cl_4$ | 55.53 | 3.50 | 55.27 | 3.41 |
| 5 | | | | 55.36 | 3.55 |
| 3a | $C_{16}H_{12}Cl_6$ | 46.09 | 2.90 | 46.27 | 3.02 |
| 3b | | | | 46.04 | 2.85 |
| 6 | | | | 45.91 | 2.77 |
| 8 | $C_{16}H_{10}Cl_6$ | 46.31 | 2.43 | 46.23 | 2.48 |
| 9 | | | | 46.19 | 2.29 |
| 4 | $C_9H_6Cl_4O_2$ | 37.54 | 2.10 | 37.35 | 2.02 |

### Acknowledgement

See the preceding paper.

### REFERENCES

[1] Md. A. Hashem, P. Weyerstahl and B.S. Green, Tetrahedron 1983, preceding paper.

[2] E. V. Dehmlow and M. Lissel, Chem. Ber. 111, 3873 (1978).