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STEREOCHEMISTRY OF BIS-(DICHLOROCYCLOPROPANATION) AND -(EPOXIDATION) OF 1,4-DIARYLBUTADIENES

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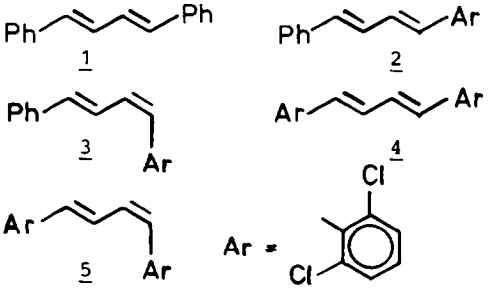
ABSTRACT - Dichlorocyclopropanation as well as epoxidation of the 1,4-diarylbutadienes 1 - 4 to give the mono- and/or bis-adducts according to several methods were studied. Dichlorocyclopropanation is more affected than epoxidation by sterical hindrance of large substituents as 2,6-dichlorophenyl. The bis-adducts are formed preferably as meso- (or threo-) isomers.

The reaction of CCl_2 with diolefins, which are capable of adding two moles of CCl_2 to give bis(dichlorocyclopropyls), have been studied primarily with dienes having alkyl substituents. In the reactions of symmetrically substituted dienes the expected meso- and d,l-diastereomers were formed, and in several cases they could be separated and their stereochemistry assigned [1]. For all the compounds thus far investigated it was found, that the meso-isomers display lower dipole moments, higher melting points, and shorter gas-chromatographic retention times than the d,l-forms.

Addition of the bulky CCl_2 group to a diene results in a monoadduct, which is highly predisposed to add a second CCl_2 group on the side opposite to that of the first addition. This results in the formation of meso, or threo-bisadducts in high yields relative to d,l-, or erythro- bisadducts.

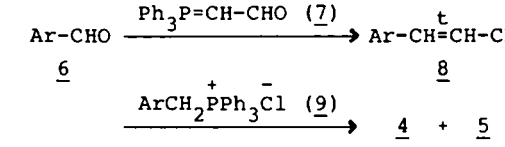
However, when CCl_2 is generated by the phase transfer method [2] it is very reactive even toward sterically hindered olefins [3]. Therefore, it appeared of interest to examine the reactions of CCl_2, generated by the phase transfer method, with a series of 1,4-diarylbutadienes which vary in degree of steric hindrance. The compounds 1 - 4 were chosen for investigation because of their accessibility, simplicity, and expected ease of comparison.

We sought to study the influence of diene substituents on the regioselectivity of monoaddition to the unsymmetrical dienes (2, 3), to examine the relative degree of bisadduct formation in the four compounds, and to estimate the meso/d,l, or threo/erythro ratios in these reactions. At the same time, it appeared useful to study the reactivity of the same four dienes in an analogous reaction, epoxidation. Here, too, three-membered ring formation takes place but the difference in size between the small oxygen atom and the large CCl_2 might provide more detailed information on the stereochemical demands of the first and second steps of bisadduct formation in the reaction of dienes.



Results and Discussion

Compounds 1-3 were known materials, but compound 4, not previously prepared, was synthesized by two Wittig reactions. 2,6-Dichlorobenzaldehyde (6) was treated with the stabilized ylid 7[4] to give 2,6-dichloro cinnamaldehyde (8) which was converted with 2,6-dichlorobenzyl triphenylphosphonium chloride (9) to a readily separable mixture of 83% 4 and 7% 5.

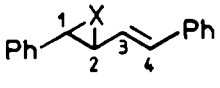


6 8

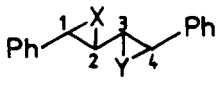
The addition of CCl_2 to 1 has been carried out in two ways: with a slight excess of $HCCl_3$ in CH_2Cl_2 as a solvent (method A), and with a large excess of $HCCl_3$ which also served as solvent (method B). The results, summarized in Table 1, show that formation of mono- or bisadduct is strongly dependent on the amount of $HCCl_3$.

Table 1. Dependence of CCl_2-mono (10), meso-bis (11a), and d,l-bisadducts (11b) on reaction conditions

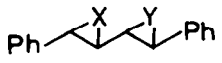
method	isolated yield, %		
	10	11a	11b
A	65	14	0
B	6	61	12



10: X = CCl_2
12: X = O



11a, 13a, 16a

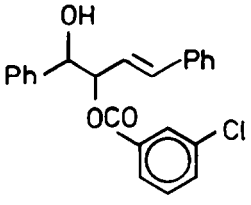


11b, 13b, 16b

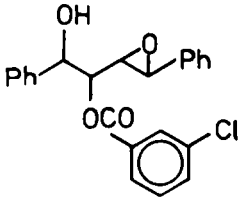
	X	Y
11a, 11b	CCl_2	CCl_2
13a, 13b	O	O
16a, 16b	CCl_2	O

The dipole moments of 11a (1.1 D) and 11b (2.5 D), and the melting points (see Table 2) are consistent with the stereochemical assignment. The ^{1}H-NMR spectra show a downfield shift of about 0.5 ppm for 2-H of 11b in comparison to 11a, because the main conformation of 11b pushes 2-H to the deshielding area of the chlorine atoms. This is in good agreement with observations on CCl_2-bisadducts of similar structure which have Me instead of Ph[1c].

The epoxidation reaction of 1 showed some peculiar results. Treatment of 1 with molar amounts of m-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 at 0 °C (method C) gave no trace of the monoepoxide 12, but 58% of the addition product[5] 14 and a small amount of meso-bis epoxide 13a.



14



15

However, 12 could be isolated in high yield (74%) via the biphase alkaline procedure with MCPBA and aqueous $NaHCO_3$ (method E)[6], but even in this case 8% of 14 were formed. With excess MCPBA in the usual way (method D), 84% of bisepoxide 13a was obtained (perhaps very small amounts of the d,l-isomer 13b remained in the mother liquor). The bisepoxide 13a is clearly not acid sensitive. The high reactivity of 12 with protons is readily understood by formation of a strongly stabilized cation after ring cleavage of the protonated epoxide. This driving force is absent with bisepoxide 13a. Even 14 yields a stable epoxide 15 after the usual treatment with MCPBA.

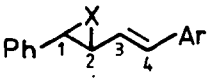
Although only one bisepoxide was isolated, its assignment as the meso-isomer 13a seems doubtless. In addition to the high melting point, 158-160 °C, the formation of one isomer is significant. Epoxidation of 10 leads to a mixture of two epoxides 16 with 54% and 28% yield. Again we assume that attack to the less hindered side should give preferably the higher melting 16a with threo- (quasi-meso) stereochemistry.

In view of the fact 10 reacts with a second CCl_2 to give a ratio of ca. 5:1 for meso/d,l bisadduct 11 formation and since it reacts with MCPBA to give the corresponding threo/erythro bisadducts 16 in a ratio of ca. 2:1, one would have expected that epoxidation of the monoepoxide, 12, would yield the analogous meso- and d,l-adducts 13a and 13b, in nearly equal amounts. However, 13b was not detected and must be formed to a much smaller degree than even 11b. It is not clear why this is so, but it may be due to the difference in the conformations of the monoolefins 10 and 12 as well as the differences in interactions of the attacking species (CCl_2 or MCPBA) with the three-membered rings already present. Further study of this point is necessary.

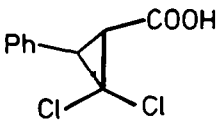
The two double bonds of diolefin 2 should differ greatly in their reactivity, because of the large steric hindrance due to 2,6-dichlorosubstitution.

Therefore it is not surprising that even with a large excess of $HCCl_3$ (method B) the monoadduct 17 is the major product. The structure of 17 was proven unambiguously by ozonolysis to give the phenylcyclopropane carboxylic acid 18 and 2,6-dichlorobenzoic acid (19).

The bisadduct 20a could be isolated in only 23% yield. Steric hindrance for formation of the erythro-isomer 20b must be too great since no trace was detected. Reaction of 2 according to method A gave a very surprising result. Instead of dichlorocyclopropanation, chlorination took place. This reaction is described in the following paper[9].

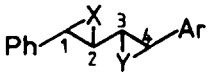


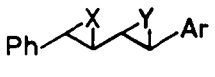
17: X = CCl_2
21: X = O



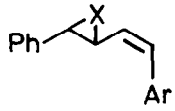
18

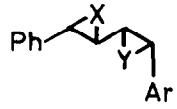
Ar-COOH
19





20a X, Y = CCl_2 20b
22a X, Y = O 22b
23a: X = CCl_2, Y = O





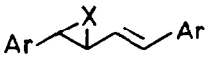
24: X = CCl_2 26a: X, Y = O
25: X = O 27a: X = CCl_2, Y = O

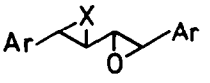
Epoxidation also showed the steric hindrance by the bulky aryl group, but again to a smaller extent. MCPBA (method C) gave, together with some starting material, 56% of the monoepoxide 21 and 4% bisepoxide 22a/b-mixture. Using method D, after 7 days of reaction, 40% 21, 26% crystalline 22a, and 19% oily 22b were isolated by chromatography. Epoxidation of the CCl_2-monoadduct 17 was achieved with an excess of MCPBA and longer reaction time to give 19% 23a as the only product, obviously with an analogous configuration.

The isolation of the (E,Z)-isomer 3 from the Wittig reaction mixture allowed us to investigate the influence of the stereochemistry of the more hindered double bond. In agreement with previous results[3c] the product ratio indicates that a strongly

hindered double bond is even less reactive as the (Z)-isomer toward CCl_2 than as the (E)-isomer. After 32 h refluxing (method B) we isolated 91% monoadduct 24 only; even with excess MCPBA after 7 days 65% monoepoxide 25 and only 4.5% bisepoxide 26a were isolated. In addition, 10% 22a was formed by isomerization of the double bond during the epoxidation procedure. Finally, the reaction of the monoadduct 24 with MCPBA illustrates the decreased reactivity of the (Z)-double bond. Under the same conditions described above, we obtained only 4% epoxide 27a, and 5% isomerized compound 23a. Repeated treatment of 24 with excess CCl_2 gave no further reaction. The starting material could be recovered.

The symmetrical diolefin 4 having two equally hindered double bonds could be converted to the monoadduct 28 in 10% yield. Most of the starting material remained, and bisadduct could not be detected.





28: X = CCl_2 30a: X = O

29: X = O 31a: X = CCl_2

Reaction with an excess of MCPBA also leads preferably to the monoepoxide 29. Repeated treatment of 29 with excess MCPBA gave, in addition to some unchanged starting material, 26% of the bisepoxide 30a, the meso-isomer. Epoxidation of 28, on the other hand, furnished the epoxide 31a in 36% yield after 14 days.

Conclusion

It is possible to determine the relative configuration of meso- and d,l-bisadducts of CCl_2 or oxygen to 1,4-diarylbutadienes by comparison of their melting points, dipole moments, ^{1}H-NMR spectra, and yields. In case both isomers are obtainable, one or two of these parameters are sufficient for an assignment. If only one isomer is formed, it will generally be the meso- (or threo-) form. Both of the reactions investigated, dichlorocyclopropanation and epoxidation, are considerably depressed by substitution with the large 2,6-dichlorophenyl group, but the dichlorocyclopropanation is affected to a much greater extent. Sterically hindered double bonds are less reactive toward these attacks in the (Z)- than in the (E)-configuration.

EXPERIMENTAL

^{1}H-NMR spectra: in $CDCl_3$, Bruker WH-270 (Me_4Si, δ = 0 ppm). ^{13}C-NMR spectra: in $CDCl_3$, Varian CFT-20. IR spectra: Perkin-Elmer 257. Dipole moments: in cyclohexane, at 20 °C, WTW-01 dipolemeter. Ozone generator: Fisher 501. - Elemental analysis: Institute of Organic Chemistry, TU Berlin [16]. - Column chromatography: on silica gel with petroleum ether/ether (P/E). - All organic phases were dried over $MgSO_4$.

(E,E)- (2) and (E,Z)-1-Phenyl-4-(2,6-dichlorophenyl)-1,3-butadiene (3)

The crude mixture obtained by reaction of cinnamyl triphenylphosphonium chloride and 2,6-dichlorobenzaldehyde (6) in presence of BuLi according to lit.[10] was chromatographed with P/E (98:2) to give 51% of 2: m.p. 107 °C (lit.[10] m.p. 107-108 °C). - ^{1}H-NMR: δ 6.75 (dd, J = 16; 10 Hz, 2-H), 6.99 (dd, J = 16; 10 Hz, 3-H), 7.09 (d, br, J = 16 Hz, 1-H), 7.11 (d, br, J = 16 Hz, 4-H), 7.35-7.55 (m, H-Ph), and 30% of 3: m.p. 32 °C (lit.[10] oily). - ^{1}H-NMR: δ 6.34 (dd, J = 10; 5 Hz, 3-H), 6.59 (dd, J = 15; 5 Hz, 2-H), 6.65 (d, br, J = 10 Hz, 4-H), 6.79 (d, br, J = 15 Hz, 1-H), 7.25-7.35 (m, H-Ph).

(E,E)- (4) and (E,Z)-1,4-Bis(2,6-dichlorophenyl)-1,3-butadiene (5)

A. 2,6-Dichlorocinnamaldehyde (8).

A solution of 2.25 g (13 mmol) 6 and 4.50 g (13.8 mmol) phosphorane 7[4] in 60 ml of benzene was refluxed for 24 h. After removal of benzene the residue was extracted with a small amount of cold ether. 3.8 g of a crude solid remained after ether evaporation and was chromatographed with P/E (96:4) to give 1.4 g (60%) of 8: m.p. 53 °C. ^{1}H-NMR: δ 6.93 (dd, J = 16; 8 Hz, 1-H), 7.3-7.4 (m, H-Ph), 7.66 (d, J = 16 Hz, 2-H), 9.73 (d, J = 8 Hz, CHO).

B. 2,6-Dichlorobenzyl triphenylphosphonium chloride (9)

Table 2. Melting points and ^{1}H-NMR spectral data[a] for mono- and bis-adducts of CCl_2 and oxygen to dienes 1 - 4

Compound	m.p. °C	Chemical shifts, δ 1-H	2-H	3-H	4-H	J, Hz $J_{1,2}$	$J_{2,3}$	$J_{3,4}$
10 [b]	oily	2.92	2.76	6.15	6.77	8	8	16
11a [b,c]	186 [d]	2.82	1.92	1.92	2.82	6	0	6
11b [b,c]	110 [e]	2.78	2.45	2.45	2.78	7	0	7
12 [b]	60—63 [f]	3.90	3.33	6.08	6.83	2	8	16
13a [b,c]	158-160 [g]	3.93	3.19	3.19	3.93	1	0	1
16a [b]	103	3.00	2.36	3.37	3.82	8	3.5	2
16b [b]	64	2.88	2.12	3.20	3.95	8	7	2
17 [h]	75—77	2.96	2.82	6.27	6.79	8	8	16
20a [b]	139-142	2.88	2.08	2.55	3.06	8.5	7	8.5
21 [h]	42—44	3.90	3.59	6.23	6.87	2	7	16
22a [h]	77	4.04	3.36	3.48	4.04	2	3.5	2
22b [h]	oily	4.03	3.32	3.40	4.06	2	3.5	2
23a [b]	135	3.05	2.58	3.66	3.88	8	2.5	2
24 [h]	oily	2.81	2.40 [i]	5.90	6.59 [i]	8	8	11
25 [h]	85	3.88	3.23	5.76	6.60	2.5	9	11
26a [h]	145	3.93	2.61	3.36	4.19	2	6.5	4
27a [h]	oily	2.72	2.18	3.86	4.20	8	2	3.5
28 [b]	112-114	2.79	2.98	6.25	6.86	8	8	16
29 [b]	184-186	4.02	3.77	6.28	6.98	2	7	16
30a [b,c]	172-175	4.18	3.56	3.56	4.18	1	0	1
31a [h]	167-169	2.87	2.31	3.34	4.29	8	8	2

[a] 270 MHz, in $CDCl_3$, in ppm relative to TMS; for numbering see formula. - [b] The aromatic protons show multiplets from 7.25-7.35. [c] These spectra are of the AA'BB'-type; interpretation by first order analysis is possible at 270 MHz. - [d] Lit.[3a] m.p. 179 °C. - [e] Lit.[3a] m.p. 110 °C. - [f] Lit.[7] m.p. 73.5 °C. - [g] Lit.[8] m.p. 165-167 °C. - [h] The aromatic protons show multiplets from 7.15-7.35. - [i] Allylic coupling of 1 Hz.

Satisfactory analytical data were reported for all new compounds listed in the table (see [16]).

A mixture of 40.0 g (155 mmol) Ph_3P, 29.0 g (149 mmol) 2,6-dichlorobenzyl chloride[11] and 15 ml of benzene was refluxed for 1 h. After cooling the solid was washed repeatedly with ether to remove starting material. Recrystallization from $CHCl_3$ gave 60.0 g (88%) 9: m.p. 268 °C.

C. Wittig reaction in two phase system[12] of 8 with 9

7.5 ml of 50% aq. NaOH were slowly added to a stirred mixture of 7.0 g (16 mmol) 9 and 3.0 g (15 mmol) 8 in 10 ml of CH_2Cl_2, after 40 min 100 ml of CH_2Cl_2 and 75 ml of water were added, and after shaking, the phases were separated. After removal of the CH_2Cl_2 the residue (9.0 g) was dissolved in 30 ml of warm EtOH. After 6 h in the refrigerator, the crystals were filtered and dried to give 1.73 g (83%, regarding the converted 8) of 4: m.p. 161 °C. - ^{1}H-NMR: δ 6.83, 7.14 (AA'BB'-system, 1-,2-,3-,4-H), 7.3-7.4 (m, H-Ph).

The concentrated mother liquor of 4 was treated with cold petroleum ether to remove Ph_3PO, after evaporation, the residue was chromatographed with P/E (95:5). Besides 1.8 g unreacted 8 as 2nd fraction, 0.15 g (7%) isomer 5 was isolated as 1st fraction, m.p. 82-85 °C. - ^{1}H-NMR: δ 6.34 (dd, J = 10; 7 Hz, 3-H), 6.45 (d, J = 10 Hz, 4-H), 6.67, 7.29 (m, 1-, 2-H), 7.3-7.4 (m, H-Ph).

General Procedure for the Generation of CCl_2 (Dichlorocyclopropanation) Method A (slight excess).

6 ml of 50% aq. NaOH were slowly dropped to a stirred mixture of 5mmol diolefin, 8 ml of $CHCl_3$, 0.2 g benzyltriethylammonium chloride (BTEAC) and 50 ml of CH_2Cl_2 at room temp. After 4 h refluxing and stirring over night at room temp. the mixture was diluted with 500 ml of water and separated. The aqueous layer was extracted with a small portion of CH_2Cl_2, and the combined organic phases were washed with water. After removal of the solvent, the residue was purified by distillation, crystallization, or chromatography.

Method B (large excess).

25 ml of 50% aq. NaOH were slowly dropped to a stirred soln of 5 mmol of diolefin, 0.2 g BTEAC, and 60 ml of $CHCl_3$, further reaction and work up as described under method A.

General Procedure for the Epoxidation with m-Chloroperbenzoic Acid (MCPBA). Method C (molar amounts).

A soln of 1.8 g (10.5 mmol) MCPBA in 80 ml of dry CH_2Cl_2 was slowly dropped under ice cooling to a soln of 10 mmol of diolefin in 50 ml of dry CH_2Cl_2. After stirring 4 h at 0 °C and 12 h at room temp., the mixture was thoroughly washed with saturated solns of $NaHSO_3$, $NaHCO_3$, and NaCl. After removal of the solvent under reduced pressure, the residue was purified as described below.

Method D (excess MCPBA).

A soln of 2,0 g (12 mmol) MCPBA in 75 ml of dry CH_2Cl_2 was slowly added under ice cooling to a soln of 5 mmol of diolefin in 25 ml of dry CH_2Cl_2. Thereafter the mixture was stored in a refrigerator for 24 h and again stirred for 12 h (or longer, see below) at room temp. Work up as descibed under method C.

Method E (alkaline biphase solvent system).

0.86 g (5 mmol) MCPBA were slowly added to a stirred mixture of 5 mmol of diolefin and 15 ml of 0.5 M aq. $NaHCO_3$. After 24 h stirring at room temp., the organic phase was separated and successively washed with 30 ml of 1 N aq. NaOH (twice) and 50 ml of water. Further work up as desribed under method C.

1,1-Dichloro-t-2-phenyl-r-3-[(E)-2'-phenylethen-1'-yl]cyclopropane (10)

From 1.03 g 1[11] according to method A. The crude product (2.4 g) was chromatographed with P/E (97:3) to give 0.23 g 1, 0.43 g (14%) bisadduct 11a, and 0.70 g (65%) 10 as a viscous oil 3rd fraction). ^{13}C-NMR[13]: δ 38.4 (d, C-3), 42.1 (d, C-2), 65.9 (s, C-1).

meso- (11a) and d,l-2,2'-Bi(1,1-dichloro-t,t-3,3-diphenylcyclopropyl) (11b)

From 1.03 g 1, method B. The crude product (2.35 g was fractionally crystallized from ether to give 1.03 g (61%) 11a. The combined mother liquors were chromatographed with P/E (97:3) to give 0.05 g 1, 0.01 g 11a, and 0.32 g of a mixture, which was repeatedly chromatographed to yield 0.08 g (6%) 10 and 0.22 g (12%) 11b. - 11a [11b]: ^{13}C-NMR: δ 35.5 [34.6] (d, C-2), 41.5 [40.7] (d, C-3), 64.3 [64.1](s, C-1). - Dipole moment: 11a [11b]: 1.08 D [2.53 D].

t-2-Phenyl-r-3-[(E)-2'-phenylethen-1'-yl]-oxirane (12)

From 1.03 g 1, method E. The crude product (1.05 g) was recrystallized twice from P/E (95:5) to give 0.82 g (74%) 12. - ^{13}C-NMR: δ 60.7 (d, C-2), 62.9 (d, C-3). - The mother liquors contain mostly compound 14.

meso-2,2'-Bi(t,t-3,3-diphenyloxiranyl) (13a)

From 1.03 g 1, method D. The crude product (1.7 g) was dissolved in P/E (7:3) and stored for 5 d in a refrigerator. 0.98 g (85%) bisepoxide 13a were isolated. - ^{13}C-NMR: δ 56.8 (d, C-2), 60.5 (d, C-3).

1,4-Diphenyl-(E)-3-butene-1,2-diol-1-m-chlorobenzoate (14)

From 3.09 g 1, method C. The crude product (5.0 g) was chromatographed with P/E (3:1) to give 0.6 g 1, 0.06 g (2%) 13a and 2.8 g colourless crystals. After recrystallization from ether 2.56 g (58%) of 14 were isolated, m.p. 91 °C. - IR: 3600 (OH), 1730 cm^{-1} (CO). - ^{1}H-NMR: δ 2.50 (d, J = 4 Hz, OH), 5.00 (dd, J = 6 ; 4 Hz, 1-H), 5.87 (dd, J = 7; 6 Hz, 2-H), 6.12 (dd, J = 16; 7 Hz, 3-H), 6.63 (d, J = 16 Hz, 4-H), 7.4-8.0 (m, H-Ph). - ^{13}C-NMR: δ 75.9 (d, C-1), 79.0 (d, C-2), 164.6 (s, CO).

t-2-(1'-m-Chlorobenzoyloxy-2'-hydroxy-2'-phenylethyl)-r-3-phenyloxirane (15)

From 2.2 g (6 mmol) 14, method D, but 2 d at room temp. The crude product (2.0 g) was chromatographed with P/E (1:1) to give 0.6 g 14, and 1.20 g (72%) 15, m.p. 135-138 °C (from ether/CH_2Cl_2 1:1). - IR: 3605 (OH), 1730 cm^{-1} (CO). - ^{1}H-NMR: δ 2.60 (d, J = 2 Hz, OH), 3.07 (dd, J = 6; 2 Hz, 2-H), 3.50 (d, J = 2 Hz, 3-H), 5.06 (dd, J = 8; 2 Hz, 2'-H), 5.32 (dd, J = 8; 6 Hz, 1'-H), 7.0-8.1 (m, H-Ph). - ^{13}C-NMR: δ 57.1 (d, C-2), 60.9 (d, C-3),. 74.5 (d, C-2'), 78.3 (d, C-1'), 165.1 (s, CO).

threo- (16a) and erythro-t-2-(1',1'-Dichloro-t-3'-phenylcycloprop-r-2'-yl)-r-3-phenyloxirane (16b)

From 2.88 g (10 mmol) 10 and 1.80 g

(15 mmol) MCPBA, method D, 36 h at room temp. The crude product (3.3 g) was repeatedly chromatographed with P/E (98:2) and crystallized from P/E (8:2) to give 1.25 g (41%) 16a and 0.65 g (21%) 16b. - 16a [16b]: ^{13}C-NMR: δ 35.7 36.0 (d, C-2'), 37.3 38.7 (d, C-3'), 57.5 [57.5] (d, C-2), 58.7 [61.1](d, C-3), 63.0 [63.2] (s, C-1').

1,1-Dichloro-t-2-[(E)-2'-(2,6-dichlorophenyl)-ethen-1'-yl]-r-3-phenylcyclopropane (17).

From 1.10 g (4 mmol) 2, method B, but 15 h refluxing. The crude product (2.2 g) was chromatographed with P/E (99:1) and again with P/E (97:3). After 0.15 g 2, 0.48 g (39%) of 17 were obtained. ^{13}C-NMR: δ 36.7 (d, C-2), 42.2 (d, C-3), 65.6 (s, C-1).

threo-t-3-Phenyl-t-3'-(2,6-dichlorophenyl)-bi(1,1'-dichlorocycloprop-2-yl) (20a).

From 1.10 g (4 mmol 2, method B, but 48 h refluxing. The crude product (1.7 g) was chromatographed with P/E (99:1). After 2 days in a refrigerator, 0.41 g (23%) of 20a crystallized. ^{13}C-NMR: δ 36.0 (d, C-2), 37.8 (d, C-2'), 40.7 (d, C-3), 41.0 (d, C-3'), 64.6 (s, C-1), 65.1 (s, C-1'). - From the mother liquors 0.53 g (37%) 17 can be isolated by chromatography with P/E (99.5:0.5).

t-2-[(E)-2'-(2,6-Dichlorophenyl)ethen-1'-yl]-r-3-phenyloxirane (21).

From 275 mg (1 mmol) 2, method C. The crude product (255 mg) was chromatographed with P/E (97:3) to give 152 mg (56%) of 21. - ^{13}C-NMR: δ 60.7 (d, C-2), 62.6 (d, C-3). - 14 mg of 22a,b were obtained as 2nd fraction.

threo- (22a) and erythro-t-3-Phenyl-t-3'-(2,6-dichlorophenyl)-2,2'-bioxiranyl (22b).

From 0.55 g (2 mmol) 2, method D, 7 d at romm temp. The crude product (0.70 g) was chromatographed with P/E (95:5) to give 0.23 g 21, and 0.30 g of 22a,b. After 3 d in a refrigerator 0.14 g 22a crystallized from petroleum ether. The mother liquor was repeatedly chromatogrphed with P/E (8:2) to give further 0.02 g of 22a (total yield 26%) and 0.12 g (19%) of 22b. - 22a [22b]: ^{13}C-NMR: δ 54.0 [53.5] (d, C-2), 56.5 [56.0] (d, C-2'), 58.6 [58.3] (d, C-3), 59.9 [59.6] (d, C-3').

t-2R*-(1',1'-Dichloro-t-3'-phenylcycloprop-r-2'R*-yl)-r-3-(2,6-dichlorophenyl) oxirane (23a).

From 0.36 g (1 mmol) 17, method D, 7 d at room temp. The crude product (0.35 g) was dissolved in P/E (95:5). After 1 d in a refrigerator, 72 mg (19%) 23a crystallized. - ^{13}C-NMR: δ 35.3 (d, C-2'), 36.3 (d, C-3'), 55.2 (d, C-2), 56.5 (d, C-3), 63.0 (s, C-1'). - From the mother liquor 0.26 g 17 could be obtained.

1,1-Dichloro-t-2-[(Z)-2'-(2,6-dichlorophenyl)ethen-1'-yl]-r-3-phenylcyclopropane (24).

From 1.10 g (4 mmol) 3, method B, 32 h refluxing. The crude product (1.8 g) was chromatographed with P/E (98:2) to give 1.3 g (91%) of 24. - ^{13}C-NMR: δ 34.8 (d, C-2), 42.6 (d, C-3), 65.6 (s, C-1).

t-2-[(Z)-2-(2,6-Dichlorophenyl)ethen-1-yl]-r-3-phenyloxirane (25) and threo-t-3-Phenyl-c-3'-(2,6-dichlorophenyl)-2,2'-bioxiranyl (26a).

From 1.10 g (4 mmol) 3, method D, 7 d at room temp. The crude product (1.3 g) was chromatographed with P/E (95:5) to give 0.76 g 25; ^{13}C-NMR: δ 59.6, 59.7 (d, C-2, -3), and 0.19 g of a 22a/26a mixture. This was dissolved in ether and petroleum ether was added until the soln becomes cloudy. After standing overnight in a refrigerator 54 mg (4.5%) of crystalline 26a were obtained. - ^{13}C-NMR: δ 54.4 (d, C-2), 56.0 (d, C-2'), 57.3 (d, C-3), 59.9 (d, C-3'). - The mother liquor contains 0.12 g (10%) 22a.

c-2R*-(1',1'-Dichloro-t-3'-phenylcycloprop-r-2'R*-yl)-r-3-(2,6-dichlorophenyl)oxirane (27a).

From 1.07 g (3 mmol) 24, method D, 7 d at room temp. The crude product (1.05 g) was chromatographed with P/E (97:3) to give 0.75 g 24, 43 mg (4%) 27a; ^{13}C-NMR: δ 33.5 (d, C-2'), 36.8 (d, C-3'), 54.1 (d, C-2), 54.8 (d, C-3), 63.1 (s, C-1'); and 0.12 g of a mixture. The latter was treated with ether and stored for 3 weeks in a refrigerator. Thereafter 55 mg (5%) of 23a could be isolated.

1,1-Dichloro-t-2-[(E)-2'-(2,6-dichlorophenyl)ethen-1'-yl]-r-3-(2,6-dichlorophenyl)-cyclopropan (28).

From 1.03 g (3 mmol) 4, method B, 24 h refluxing. The crude product (1.1 g) was chromatographed with P/E (97:3) to give 0.72 g 4, and 0.13 g (10%) of 28. - ^{13}C-NMR: δ 40.2 (d, C-2), 42.1 (d, C-3), 66.1 (s, C-1).

t-2-[(E)-2'-(2,6-Dichlorophenyl)-ethen-1'-yl]-r-3-(2,6-dichlorophenyl)oxirane (29).

From 1.03 g (3 mmol) 4, method D, 5 d at room temp. Recrystallization of the crude product (1.1 g) from CH_2Cl_2/ether (1:1) gave 0.98 g (85%) of 29.

meso-2,2'-Bi[(t,t-3,3'-bis(2,6-dichlorophenyl)]oxiranyl (30a).

From 0.72 g (2 mmol) 29, method D, 15 d at room temp. The crude product (0.52 g) was chromatographed with P/E (9:1) to give 0.21 g 29, and 0.21 g (26%) of 30a.- ^{13}C-NMR: δ 53.5 (d, C-2), 58.3 (d, C-3).

threo-t-2-[1',1'-Dichloro-t-3'-(2,6-

-dichlorophenyl)-cycloprop-r-2'-yl)]--r-3-(2,6-dichlorophenyl)oxirane (31a).

From 80 mg (0.2 mmol) 28 and 172 mg (1.0 mmol) MCPBA, method D, 14 d at room temp. The crude product (80 mg) was chromatographed with P/E (9:1) to give 30 mg (36%) of 31a.

Ozonolysis of 17.

A soln of 0.18 g (0.5 mmol) 17 in 70 ml of dry $CHCl_3$ was at -10 °C continuously treated with a flow of O_2/O_3 (3.5 g O_3/h) for 30 min. After removal of the solvent in vacuo, 20 ml of 30% H_2O_2 was given to the residue, and after addition of 25 ml of water the mixture was stirred for 30 min. Then 10 ml of HCOOH were added, and the soln was carefully heated up to 50 °C. After completion of the vigorous reaction, it was refluxed for 1 h. The cooled soln was extracted several times with 25 ml portions of ether, the ethereal soln was washed with water. After removal of the solvent the crude product (0.14 g) was chromatographed with P/E (1:1) to give 27 mg (28%) of 2,6-Dichlorobenzoic acid (19) m.p. 139-142 °C (lit.[14] m.p. 141-142 °C), and 52 mg (43%) of 1,1-Dichloro-t-3-phenylcyclopropane-r-2-carboxylic acid (18), m.p. 97-99 °C (lit.[15] m.p. 101 °C); ^{1}H-NMR: δ 2.88 (d, J = 9 Hz, 2-H), 3.55 (d, J = 9 Hz, 3-H), 7.4 (m, H-Ph), 10.6 (s, COOH).

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16)

Analyses		Calculated		Found	
		C	H	C	H
4	$C_{16}H_{10}Cl_4$	55.85	2.93	55.63	2.86
5				55.71	2.97
8	$C_9H_6Cl_2O$	53.77	3.01	53.89	3.12
9	$C_{25}H_{20}Cl_3P$	65.60	4.40	65.37	4.29
10	$C_{17}H_{14}Cl_2$	70.60	4.88	70.46	4.75
14	$C_{23}H_{19}ClO_3$	72.92	5.06	73.07	5.13
15	$C_{23}H_{19}ClO_4$	69.96	4.85	70.14	4.97
16a, 16b	$C_{17}H_{14}Cl_2O$	66.90	4.62	66.68	4.50
				66.95	4.49
17	$C_{17}H_{12}Cl_4$	57.02	3.38	56.88	3.32
24				57.20	3.47
20a	$C_{18}H_{12}Cl_6$	49.02	2.74	48.94	2.65
21	$C_{16}H_{12}Cl_2O$	66.00	4.15	65.83	4.01
25				65.91	4.06
22a	$C_{16}H_{12}Cl_2O_2$	62.56	3.94	62.30	3.82
22b				62.47	3.79
26a				62.68	3.99
23a, 27a	$C_{17}H_{12}Cl_4O$	54.58	3.23	54.51	3.17
				54.44	3.12
28	$C_{17}H_{10}Cl_6$	47.82	2.36	47.73	2.31
29	$C_{16}H_{10}Cl_4O$	53.37	2.80	53.20	2,78
30a	$C_{16}H_{10}Cl_4O_2$	51.10	2.68	51.02	2.71
31a	$C_{17}H_{10}Cl_6O$	46.09	2.28	45.97	2.23