

Photochemical Reduction of *gem*-Dihalocyclopropanes. III.[†] Debromination of Some Compounds Containing Two 1,1-Dibromocyclopropane Moieties

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2,2,2',2'-Tetrabromo-1-phenylbicyclopropyl and 1,1-dibromo-2-(2,2-dibromocyclopropyl)methyl-2-phenylcyclopropane have been synthesized, analyzed by X-ray crystallographic techniques, and exposed to acetone-sensitized irradiation. The former compound, which was obtained as a single diastereoisomer, gave a product mixture consisting of an undisclosed number of the corresponding tribromides resulting from reduction at either ring. The latter tetrabromide was separated into its diastereoisomers, which were irradiated separately. One of the diastereoisomers gave a mixture of tribromides caused by reduction at either ring, whereas the other isomer was reduced regioselectively at the phenyl-substituted ring and gave a mixture of *cis*- and *trans*-1-bromo-2-(2,2-dibromocyclopropyl)methyl-2-phenylcyclopropane.

When exposed to light passing through a Pyrex filter, substituted 1-aryl-2,2-dibromocyclopropanes are converted into the corresponding monobromides.¹ The yields are rather low under direct irradiation, but improve and become, in most cases, very good when acetone-sensitization is applied.¹ Independent of the mode of irradiation the monobromides are formed as mixtures of the corresponding *cis* and *trans* isomers;¹ this is due to the fact that cyclopropyl radicals are involved as intermediates as verified by a trapping experiment.²

The formation of a cyclopropyl-radical intermediate in the reaction is believed to require efficient transfer of excitation energy from the aryl group, in a triplet-excited state, to the nearest bromine atom, i.e. the bromine *cis* to the aryl group.¹ Of the evidence supporting such a step is the observation that the efficiency of the photo-reduction drops significantly when the distance from the aryl group to the *gem*-dibromo moiety increases. Specifically, the yield of monobromide drops tenfold when the phenyl group in 1,1-dibromo-2-phenylcyclopropane is replaced by a benzyl group and the compounds are irradiated under standard reaction conditions.¹

An interesting corollary emerges from this observation: if a compound, containing two *gem*-dibromocyclopropyl groups *as well as* one phenyl group, is irradiated under

appropriate conditions, the bromine atom closest to the phenyl group should primarily be excited leading to a regioselective monoreduction of one of the *gem*-dibromo moieties. In order to see whether this proposed outcome could be achieved we made three such compounds and photolyzed them using acetone as sensitizer. The results of this investigation are reported here.

Experimental

General. UV spectra were obtained on a Varian Cary 3 UV–VIS spectrophotometer using ethanol (96%) as the solvent. IR spectra were recorded on a Perkin–Elmer 1310 infrared spectrophotometer. Absorption intensities are described as strong (s), medium (m) and weak (w). NMR spectra were run on Bruker Spectrospin AC-200 F and DRX 600 spectrometers, which are 200 and 600 MHz, respectively, in proton and 50 and 150 MHz, respectively, in carbon. CDCl₃ and CCl₄ were used as solvents with added tetramethylsilane (TMS) as an internal reference. Chemical shifts are reported downfield from TMS and coupling constants (*J*) are given in Hz. The multiplicity of the signals is characterized as (s) for singlet, (d) for doublet, (t) for triplet, (q) for quartet and (m) for multiplet. GC analyses were performed on an HP 5720A gas chromatograph equipped with FID and a 15% SP 2100 Supelcoport column and connected to an HP 3395 integrator. No corrections were made for response ratios. Purification by flash chromatography

[†] Part II, see Ref. 1.

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was carried out with Silica gel (230–400 mesh) as the stationary phase and hexane as the mobile phase. Mass spectra were obtained on a VG 7070 Micromass spectrometer operated in the EI mode at 70 eV. The spectra are reported as m/z (% rel. int.). Melting points were determined on a Gallenkamp apparatus. Boiling points and melting points are uncorrected. Elemental analyses were performed by Ilse Betz Microanalytical Laboratory, Kronach, Germany.

Solvents. DMSO was dried with CaCl_2 and subsequently distilled. Diethyl ether was dried with sodium wire whereas THF was distilled from sodium–benzophenone. Absolute ethanol and acetone (HPLC quality) were used without further purification.

1,1-Dibromo-2-(1-phenylethenyl)cyclopropane was prepared from 1-(2,2-dibromocyclopropyl)-1-phenyl-1-ethanol³ (0.55 g, 1.7 mmol) which was dissolved in benzene (100 ml) containing a catalytic amount of TsOH and refluxed at 50 °C/150 mmHg for 3.5 h in a flask attached to a Dean–Stark trap. Water (30 ml) was added, the mixture was extracted with diethyl ether, and the combined extracts were washed with a saturated ammonium chloride solution and dried (MgSO_4). Purification by flash chromatography gave 0.45 g (87%) of the title compound. IR (film): 1615 (w), 1565 (w), 1485 (m), 1435 (m), 1418 (m), 1365 (m), 1252 (w), 1110 (m), 1052 (m), 1020 (w), 933 (w), 900 (m), 770 (s), 692 (s) cm^{-1} . ¹H NMR (200 MHz, CCl_4): δ 1.80 (1 H, dd, J 7.5 and 8.3), 1.95 (1 H, dd, J 10.0 and 7.5), 2.52 (1 H, m), 4.94 (1 H, d, J 1.48), 5.66 (1 H, d, J 0.75), 7.24–7.37 (3 H, m), 7.50–7.54 (2 H, m). ¹³C NMR (50 MHz, CCl_4): δ 26.1, 28.1, 36.1, 113.7 (CH_2), 125.7 (2 CH), 127.7 (CH), 128.2 (2 CH), 138.5 (C), 143.2 (C).

2,2,2',2'-Tetrabromo-1-phenylbicyclopropyl (1) was prepared from 1,1-dibromo-2-(1-phenylethenyl)cyclopropane (0.8 g, 2.5 mmol) with bromoform (21.0 g, 83.3 mmol), triethyl(benzyl)ammonium chloride (TEBA) (1.5 g), ethanol (0.3 ml), dichloromethane (1 ml) and 50% aqueous sodium hydroxide solution (1.0 g, 12.5 mmol) following Makoza's method.⁴ The mixture was stirred for 48 h, acidified with hydrochloric acid (6 M), and extracted with dichloromethane. The combined extracts were dried (MgSO_4). Purification by flash chromatography gave 1.07 g (91%) of **1**. UV [96% ethanol; λ (ϵ): 242 (1490), 259 (590) nm. IR (film): 1590 (m), 1573 (w), 1488 (m), 1438 (s), 1355 (w), 1245 (w), 1203 (m), 1112 (m), 1095 (m), 1070 (s), 1050 (s), 1020 (s), 980 (s), 912 (m), 890 (w), 758 (s), 695 (s), 680 (s), 620 (s) cm^{-1} . ¹H NMR (600 MHz, CDCl_3): δ 1.44 (1 H, t, J 8.3), 1.78 (1 H, d, J 9.0), 1.98 (1 H, dd, J 10.6 and 8.4), 2.31 (1 H, dd, J 8.9 and 0.8), 2.67 (1 H, dd, J 10.6 and 8.1), 7.35–7.46 (5 H, m). ¹³C NMR (50 MHz, CCl_4): δ 24.4, 29.1, 29.2, 31.5, 37.5, 38.7, 127.5 (CH), 128.0 (2 CH), 128.8 (2 CH), 138.6 (C). Molecular weight: calculated for $\text{C}_{12}\text{H}_{14}\text{Br}_4$ 475.74585; found 475.7431.

1,1-Dibromo-2-(2,2-dibromocyclopropylmethyl)-2-phenylcyclopropane (2) was synthesised from 2-phenyl-1,4-pentadiene⁵ (4.0 g, 28 mmol), bromoform (37.7 g, 139 mmol), TEBA (2.0 g), ethanol (1.0 ml) and 50% aqueous sodium hydroxide solution (13.4 g, 166 mmol) following Makosza's procedure.⁴ The reaction was stirred for two days after which additional bromoform (63.9 g, 240 mmol), ethanol (1.0 ml) and 50% aqueous sodium hydroxide solution (22.6 g, 280 mmol) were added. The resulting mixture was stirred for another four days before it was acidified with hydrochloric acid (6 M) and worked up in the usual way. Evaporation of the solvent gave 5.8 g of a crude product which contained at least four products according to TLC and NMR analyses. Two of the products, which proved to be diastereomers of **2**, were isolated and purified by flash chromatography. Diastereoisomer **A** (R_f 0.16 on silica with hexane as the eluent) was isolated in 8% yield (1.0 g) whereas diastereoisomer **B** (R_f 0.12 on silica with hexane as the eluent) was isolated in 14% yield (1.8 g).

2A: White, crystalline material, m.p. 71–72 °C (from hexane). UV [96% ethanol; λ (ϵ): 245 (890), 259 (585), 265 (374) nm. IR (CCl_4): 3092 (w), 3068 (w), 3035 (w), 2928 (w), 1609 (w), 1501 (m), 1453 (m), 1431 (m), 1222 (w), 1133 (w), 1114 (m), 1050 (m), 707 (s), 701 (s), 682 (s) cm^{-1} . ¹H NMR (600 MHz, CDCl_3): δ 0.99 (1 H, dd, J 7.6 and 7.4), 1.45–1.57 (2 H, m), 2.10 (1 H, dd, J 7.6 and 7.4), 2.12 (1 H, d, J 7.6), 2.17 (1 H, dd, J 7.7 and 1.2), 2.34 (1 H, ddd, J 14.6, 5.8 and 1.0), 7.31–7.33 (3 H, m), 7.38–7.40 (2 H, m). ¹³C NMR (50 MHz, CDCl_3): δ 28.1, 28.3, 29.7, 33.1, 35.1, 38.8, 42.8, 127.6 (CH), 128.4 (2 CH), 129.5 (2 CH), 139.9 (C). Anal. $\text{C}_{13}\text{H}_{12}\text{Br}_4$: C, H.

2B: White, crystalline material, m.p. 92–93 °C (from hexane). UV [96% ethanol; λ (ϵ): 240 (1300), 258 (910), 265 (668) nm. IR (CCl_4): 3087 (w), 3061 (w), 3030 (w), 1602 (w), 1494 (m), 1444 (m), 1425 (m), 1210 (m), 1114 (m), 1095 (m), 1051 (m), 1019 (w), 985 (w), 702 (s), 676 (s) cm^{-1} . ¹H NMR (600 MHz, CDCl_3): δ 1.11 (1 H, t, J 7.7), 1.50–1.56 (1 H, m), 1.70 (1 H, dd, J 10.3 and 7.3), 1.80 (1 H, dd, J 14.5 and 8.4), 1.85 (1 H, d, J 7.6), 2.13 (1 H, dd, J 7.6 and 1.1), 2.70 (1 H, dd, J 14.5 and 5.3), 7.31–7.33 (3 H, m), 7.37–7.40 (2 H, m). ¹³C NMR (50 MHz, CDCl_3): δ 27.6, 28.2, 29.2, 33.1, 34.5, 38.7, 42.9, 127.6 (CH), 128.3 (2 CH), 129.5 (2 CH), 139.7 (C). Anal. $\text{C}_{13}\text{H}_{12}\text{Br}_4$: C, H.

Structure determination by X-ray crystallography. Crystals of the two diastereoisomers of 1,1-dibromo-2-(2,2-dibromocyclopropylmethyl)-2-phenylcyclopropane, **2A** and **2B**, suitable for X-ray experiments were obtained by recrystallization of the isomers from hexane. Colorless, irregular crystals were cut to prismatic specimens with the approximate dimensions of 0.25 mm \times 0.25 mm \times 0.25 mm.

The cell dimensions were measured and the intensity data were collected on an Enraf–Nonius CAD4-diffractometer using graphite-monochromated $\text{Mo K}\alpha$

radiation ($\lambda=0.71073 \text{ \AA}$). The crystal temperature was approximately 110 K during the data collection. The cell parameters were determined using a least-squares fit of 25 reflections. The intensities of three reflections were measured at 2 h intervals, and a correction for a linear intensity decrease of approximately 8% for **2A** and 2% for **2B** was made. Owing to the irregular shapes of the crystals empirical absorption correction was unsuccessful. A semiempirical absorption correction was applied, which did not improve the final figures of merit; thus, the results presented are based on the uncorrected data. Details of experimental and crystal data are listed in Table 1.

The structures were solved by direct methods using SHELXS86.⁶ Subsequent refinement was carried out by Fourier and least-squares calculations using SHELXL93.⁷ The non-hydrogen atoms were treated anisotropically, while the geometrically placed hydrogen atoms were refined isotropically using a riding model. Final atom coordinates and equivalent isotropic displacement parameters are listed in Table 2. Bond lengths, bond angles and selected torsion angles derived from the

Table 1. Crystal and experimental data.

	2A	2B
Empirical formula	C ₁₃ H ₁₂ Br ₄	C ₁₃ H ₁₂ Br ₄
Formula weight	487.87 g mol ⁻¹	487.87 g mol ⁻¹
Temperature	293(2) K	109(2) K
Radiation wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
Unit cell dimensions	$a = 15.081(3) \text{ \AA}$, $\alpha = 90^\circ$ $b = 7.890(2) \text{ \AA}$, $\beta = 1.54(3)^\circ$ $c = 12.427(2) \text{ \AA}$, $\gamma = 90^\circ$	$a = 6.4510(10) \text{ \AA}$, $\alpha = 90^\circ$ $b = 12.681(3) \text{ \AA}$, $\beta = 95.82(3)^\circ$ $c = 17.809(4) \text{ \AA}$, $\gamma = 90^\circ$
Volume	1478.1(5) Å ³	1449.4(5) Å ³
Z	4	4
Density (calculated)	2.192 Mg m ⁻³	2.236 Mg m ⁻³
Absorption coefficient	10.867 mm ⁻¹	11.083 mm ⁻¹
$F(000)$	920	920
θ range for data collection	2.91–26.27°	2.80–25.97°
Index ranges	$0 \leq h \leq 18$, $-9 \leq k \leq 9$, $-15 \leq l \leq 15$	$-7 \leq h \leq 7$, $0 \leq k \leq 15$, $-21 \leq l \leq 0$
Reflections collected	5638	1677
Independent reflections	2937	1677
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	2937/0/154	1677/0/154
Goodness-of-fit on F^2	1.038	1.039
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0579$, $wR2 = 0.1255$	$R1 = 0.0443$, $wR2 = 0.1247$
R indices (all data)	$R1 = 0.1084$, $wR2 = 0.1488$	$R1 = 0.0645$, $wR2 = 0.1448$
Largest diff. peak and hole	1.746 and $-1.889 \text{ e \AA}^{-3}$	0.904 and $-0.688 \text{ e \AA}^{-3}$

Table 2. Atomic fractional coordinates and U_{eq}^a

Atom	x	y	z	U_{eq}
2A				
Br(2)	4545(1)	-2007(1)	-4251(1)	36(1)
Br(1)	5226(1)	-1896(1)	-1820(1)	33(1)
Br(3)	2959(1)	3015(1)	120(1)	38(1)
Br(4)	983(1)	1640(1)	174(1)	34(1)
C(1)	4197(5)	-2038(12)	-2784(6)	35(2)
C(2)	3424(5)	-3074(11)	-2477(7)	35(2)
C(3)	3364(5)	-1144(11)	-2514(6)	31(2)
C(4)	3261(5)	-137(11)	-1486(6)	31(2)
C(5)	2286(5)	278(10)	-1349(6)	29(2)
C(6)	1959(5)	1968(10)	-1836(6)	31(2)
C(7)	2044(5)	1758(9)	-637(6)	27(2)
C(8)	1694(5)	-1259(11)	-1391(6)	30(2)
C(13)	1682(5)	-2335(11)	-521(7)	35(2)
C(12)	1190(6)	-3835(12)	-545(7)	40(2)
C(11)	701(5)	-4215(11)	-1495(7)	41(2)
C(10)	731(6)	-3148(12)	-2373(8)	41(2)
C(9)	1224(5)	-1652(11)	-2322(7)	35(2)
2B				
Br(1)	2483(2)	-7804(1)	-5076(1)	28(1)
Br(2)	7332(2)	-8125(1)	-4665(1)	31(1)
Br(3)	-452(2)	-7896(1)	-1851(1)	27(1)
Br(4)	717(2)	-5494(1)	-1952(1)	28(1)
C(1)	4597(18)	-8408(7)	-4393(7)	28(3)
C(2)	4210(2)	-9490(7)	-4090(6)	32(4)
C(3)	4398(18)	-8544(7)	-3564(6)	22(2)
C(4)	2454(18)	-8170(7)	-3201(7)	25(2)
C(5)	2816(18)	-7131(6)	-2794(6)	20(3)
C(6)	3835(18)	-7155(7)	-1991(6)	23(3)
C(7)	1590(2)	-6912(7)	-2133(6)	27(4)
C(8)	3336(19)	-6215(7)	-3282(6)	26(3)
C(9)	5340(2)	-5847(7)	-3277(7)	27(3)
C(10)	5794(19)	-5003(8)	-3726(7)	35(4)
C(11)	4261(17)	-4535(7)	-4188(6)	23(2)
C(12)	2164(19)	-4901(8)	-4223(7)	29(2)
C(13)	1742(17)	-5755(7)	-3762(6)	23(2)

^aC(1) and C(7) are the dibrominated carbon atoms in both **2A** and **2B**.

final atom coordinates are listed in Tables 3, 4 and 5, respectively.

General procedure for sensitized irradiation of the bis-adducts. A solution of the gem-dihalocyclopropane in absolute ethanol containing enough dry acetone to absorb all the light, was degassed with nitrogen before being irradiated with light from a 125 W medium-pressure mercury lamp. The lamp was kept in a water-cooled borosilicate well (cut-off at 265 nm). After irradiation the photolysate was diluted with diethyl ether (600 ml) and subsequently washed with water (4 × 300 ml) before being dried (MgSO₄).

Irradiation of 2,2,2'-tetrabromo-1-phenylbicyclopropyl (1). A solution of **1** (0.32 g, 0.68 mmol) in a mixture of ethanol (165 ml) and acetone (60 ml, 0.8 mol) was irradiated for 50 min. Evaporation gave 0.19 g of a crude product, which showed three dominant spots with R_f values 0.16, 0.18 and 0.20 when analyzed by TLC. After

Table 3. Bond lengths (Å).^a

Bond	2A	2B
Br(1)–C(1)	1.938(7)	1.894(14)
Br(2)–C(1)	1.910(8)	1.910(9)
Br(3)–C(7)	1.925(7)	1.919(10)
Br(4)–C(7)	1.916(8)	1.922(9)
C(1)–C(2)	1.483(11)	1.505(13)
C(1)–C(3)	1.488(11)	1.504(14)
C(2)–C(3)	1.526(12)	1.519(14)
C(3)–C(4)	1.516(11)	1.543(11)
C(4)–C(5)	1.521(10)	1.510(13)
C(5)–C(6)	1.540(11)	1.512(18)
C(5)–C(7)	1.516(10)	1.509(10)
C(5)–C(8)	1.506(11)	1.509(11)
C(6)–C(7)	1.502(10)	1.476(19)
C(8)–C(9)	1.377(11)	1.372(17)
C(9)–C(10)	1.395(12)	1.386(14)
C(10)–C(11)	1.380(13)	1.357(19)
C(11)–C(12)	1.407(11)	1.425(16)
C(12)–C(13)	1.398(13)	1.402(13)
C(8)–C(13)	1.374(12)	1.396(18)

^aC(1) and C(7) are the dibrominated carbon atoms in both **2A** and **2B**.

Table 4. Bond angles (°).^a

Angle	2A	2B
C(3)–C(1)–C(2)	61.8(6)	60.7(6)
C(3)–C(1)–Br(1)	120.0(6)	123.3(7)
C(2)–C(1)–Br(1)	119.6(6)	117.6(9)
C(3)–C(1)–Br(2)	117.7(5)	116.3(9)
Br(1)–C(1)–Br(2)	110.7(4)	112.6(5)
C(2)–C(1)–Br(2)	119.4(6)	117.0(8)
C(1)–C(2)–C(3)	59.3(5)	59.7(6)
C(1)–C(3)–C(2)	58.9(6)	59.7(6)
C(1)–C(3)–C(4)	123.0(6)	122.0(10)
C(2)–C(3)–C(4)	120.4(7)	118.9(9)
C(5)–C(4)–C(3)	109.1(6)	112.1(8)
C(7)–C(5)–C(8)	119.3(6)	118.2(7)
C(7)–C(5)–C(4)	118.7(6)	117.8(7)
C(8)–C(5)–C(4)	113.4(7)	115.4(8)
C(7)–C(5)–C(6)	58.9(5)	58.5(8)
C(8)–C(5)–C(6)	120.1(6)	117.4(9)
C(4)–C(5)–C(6)	116.3(7)	117.8(9)
C(7)–C(6)–C(5)	59.8(5)	60.7(8)
C(6)–C(7)–C(5)	61.4(5)	60.9(7)
C(6)–C(7)–Br(3)	118.0(5)	120.5(7)
C(5)–C(7)–Br(3)	120.1(5)	120.9(7)
C(6)–C(7)–Br(4)	118.5(5)	117.8(8)
C(5)–C(7)–Br(4)	119.2(5)	119.3(6)
Br(3)–C(7)–Br(4)	111.5(4)	110.0(5)
C(9)–C(8)–C(13)	120.3(8)	119.8(8)
C(9)–C(8)–C(5)	120.1(7)	121.4(11)
C(13)–C(8)–C(5)	119.4(7)	118.8(10)
C(8)–C(9)–C(10)	119.4(8)	120.9(13)
C(11)–C(10)–C(9)	120.6(8)	120.2(11)
C(10)–C(11)–C(12)	120.4(8)	120.9(8)
C(13)–C(12)–C(11)	117.7(8)	117.7(12)
C(8)–C(13)–C(12)	121.6(7)	120.4(10)

^aC(1) and C(7) are the dibrominated carbon atoms in both **2A** and **2B**.

Table 5. Selected torsion angles (°).^a

Torsion angle	2A	2B
C(1)–C(3)–C(4)–C(5)	–167.8(8)	–100.8(12)
C(3)–C(4)–C(5)–C(7)	–158.3(7)	–151.5(11)
C(3)–C(4)–C(5)–C(8)	54.2(8)	61.2(14)
C(7)–C(5)–C(8)–C(9)	112.8(8)	109.6(12)
C(4)–C(5)–C(8)–C(9)	–99.9(8)	–103.2(13)
C(7)–C(5)–C(8)–C(13)	–72.2(9)	–72.1(15)
C(4)–C(5)–C(8)–C(13)	75.0(9)	75.1(11)
C(8)–C(9)–C(10)–C(11)	1.1(12)	–1.0(14)
C(9)–C(10)–C(11)–C(12)	–2.0(12)	–0.1(14)
C(10)–C(11)–C(12)–C(13)	1.4(12)	0.2(14)
C(9)–C(8)–C(13)–C(12)	–0.8(12)	–1.8(13)

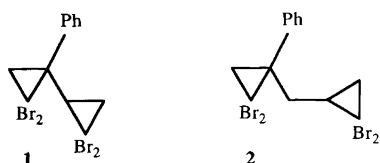
^aC(1) and C(7) are the dibrominated carbon atoms in both **2A** and **2B**.

recording the NMR spectrum of the crude product, we made several attempts to isolate pure samples of individual compounds. However, the attempts failed as judged by the NMR spectra of the isolated fractions. The total amount of the final fractions was 0.14 g, corresponding to 52% yield, provided the products are isomeric tribromides. All fractions gave essentially identical IR spectra (film): 1590 (w), 1485 (m), 1438 (m), 1251 (m), 1235 (m), 1030 (m), 752 (s), 693 (s), 610 (s) cm^{–1}. Furthermore, ¹³C NMR spectra (50 MHz, CCl₄) of all fractions gave signals in the 13–33 and 125–140 ppm regions compatible with compounds containing one or two monobromocyclopropyl moieties. The ¹H NMR spectra are discussed in the text.

Irradiation of 2A. A solution of **2A** (0.26 g, 0.55 mmol) in a mixture of ethanol (100 ml) and acetone (80 ml, 1.1 mol) was irradiated for 40 min. Evaporation gave 0.21 g of a crude product, which exhibited three dominant spots when analyzed by TLC. After recording the NMR spectrum of the crude product, we made several attempts to isolate pure samples of individual compounds. However, the attempts failed as judged by the NMR spectra of the isolated fractions. The amount of the three fractions were 50, 40, and 40 mg, corresponding to a total yield of 60% provided the products are isomeric tribromides. All fractions gave very similar IR spectra (film): 1590 (m), 1570 (w), 1482 (m), 1434 (m), 1420 (m), 1222 (m), 1100 (m), 1033 (m), 780 (m), 758 (s), 695 (s), 668 (s), 625 (s) cm^{–1}. Furthermore, the ¹³C NMR spectra (50 MHz, CCl₄) of all the fractions gave signals in the 14–45 and 125–144 ppm regions compatible with compounds containing one or two monobromocyclopropyl moieties. The ¹H NMR spectra are discussed in the text.

Irradiation of 2B. A solution of **2B** (0.48 g, 0.98 mmol) in a mixture of ethanol (90 ml) and acetone (77 ml, 1.1 mol) was irradiated for 30 min. Evaporation gave 0.36 g of a crude product, which exhibited three dominant spots when analyzed by TLC. After recording the NMR spectrum of the crude product, we made several attempts to isolate pure samples of individual compounds.

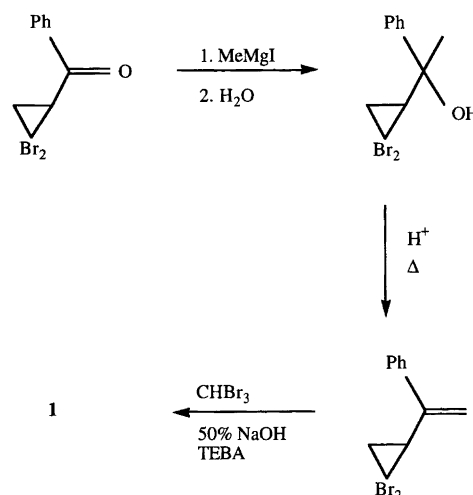
However, the attempts failed as judged by the NMR spectra of the isolated fractions. Two product fractions were isolated, weighing 80 and 21 mg, corresponding to a total yield of 73% provided the products are isomeric tribromides (see Results and discussion). All fractions gave very similar IR spectra (film): 1590 (w), 1482 (m), 1434 (m), 1250 (m), 1222 (m), 1028 (m), 755 (s), 695 (s), 676 (m), 615 (s) cm^{-1} . Furthermore, the ^{13}C NMR spectra (50 MHz, CCl_4) of the fractions gave signals in the 14–44 and 121–143 ppm regions which are compatible with compounds containing one or two monobromocyclopropyl moieties. The ^1H NMR spectra are discussed in the Results and discussion section.



Results and discussion

2,2,2',2'-Tetrabromo-1-phenylbicyclopropyl (**1**) and 1,1-dibromo-2-(2,2-dibromocyclopropylmethyl)-2-phenylcyclopropane (**2**) were chosen as model compounds for our study. With these compounds it was conceived that it would be possible to differentiate between reduction of the phenylated and the non-phenylated ring in each compound by analyzing the reaction mixtures by ^1H NMR spectroscopy. This expectation is based on two observations. Firstly, reduction of the former ring will afford an isomeric mixture of tribromides which will give ^1H NMR spectra with a double doublet (dd) for the hydrogen atom attached to the bromo-substituted carbon (one dd for the *cis* isomer and one dd for the *trans*), whereas reduction of the non-phenylated ring will furnish an isomeric mixture of tribromides whose hydrogen atom attached to the bromo-substituted carbon will appear as a multiplet (m), consisting possibly of up to eight lines (one m for the *cis* isomer and one m for the *trans*). Secondly, literature data indicate that the double doublets will appear at higher frequency than the multiplets in the ^1H NMR spectrum.^{8–10}

Synthesis. The preparation of the compounds was planned to be performed by direct addition of dibromocarbene to both C=C double bonds of the corresponding dienes, *viz.* 2-phenyl-1,3-butadiene¹¹ and 2-phenyl-1,4-pentadiene,⁵ respectively, a strategy which has considerable literature precedence.^{12–15} However, the approach turned out to be unsuccessful for the preparation of **1**, conceivably because 1,3-butadiene is rendered unreactive by the phenyl group attached to C-2; the synthesis of **1**, therefore, had to be carried out in a stepwise manner (Scheme 1). Dehydration in a Dean–Stark trap of 1-(2,2-dibromocyclopropyl)-1-phenyl-2-ethanol gave an 87% yield of 1,1-dibromo-2-(1-phenylvinyl)cyclopropane



Scheme 1.

which afforded **1** in 91% yield when exposed to a significant excess of dibromocarbene under phase-transfer conditions. The product was an oil, which appeared homogeneous by TLC under a variety of conditions, indicating that the compound is formed as a single diastereoisomer. This conclusion is supported by the ^1H and ^{13}C NMR spectra which exhibited one set of sharp, separate signals for the non-aromatic nuclei. The diastereospecific formation of **1** is therefore comparable to the specific formation of *meso* bis-adducts during the addition of dihalocarbene to 2,3-dimethyl-1,3-butadiene¹⁵ and 2,2,3,6,7,7-hexamethyl-3,5-octadiene.¹⁶

Bis-adduct **2**, on the other hand, was obtained directly from 2-phenyl-1,4-pentadiene when the diene was treated with a considerable excess of dihalocarbene under Makosza conditions, but owing to incomplete consumption of the starting material and by-product formation the yield was low. TLC analyses clearly indicated that **2** was obtained as a mixture of two diastereoisomers, and upon flash chromatography the isomers were isolated as white, crystalline materials. The diastereoisomer with the higher R_f value, denoted diastereoisomer **A** (**2A**), was isolated in 8% yield whereas the other isomer, denoted diastereoisomer **B** (**2B**), was obtained in 14% yield. Their structures were proved by spectroscopic means and subsequently confirmed by X-ray crystallographic structure analyses (*vide infra*), which also revealed the diastereoisomers' configurations.

Crystal structure of 2. As illustrated in Fig. 1, the X-ray structure investigations reveal that **2A** and **2B** are diastereoisomers. If the phenyl group were replaced by a hydrogen atom, the more abundant isomer (**2B**) would have a configuration that would give a *meso*-form. The stereoselectivity of the bis-adduct formation from 2-phenyl-1,4-pentadiene, a skipped diene, is therefore similar to that observed for 2,2,2',2'-tetrahalobicyclopropyl formation from several conjugated dienes.^{15,16}

The most apparent structural difference between **2A**

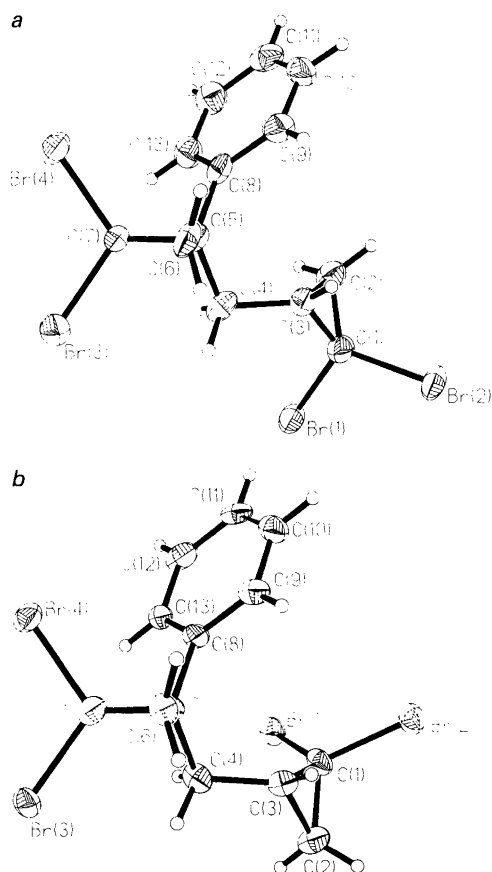


Fig. 1. ORTEP plots of the diastereomers of 1,1-dibromo-2-(2,2-dibromocyclopropylmethyl)-2-phenylcyclopropane: (a) the minor form (**2A**); (b) the major form (**2B**).

and **2B** is the position of the *gem*-dibromo moiety of the 2,2-dibromocyclopropylmethyl group relative to the phenyl ring. Whereas this group points away from the phenyl ring in **2A**, the *gem*-dibromo moiety is directed towards the ring in **2B**. As a result one bromine atom in each cyclopropyl group in **2B**, Br(1) and Br(4), are at a the same distance (3.9 Å) from the center of the phenyl ring; in **2A** only one bromine atom is at such a distance, the others are more than 5.5 Å away (Table 6).

Owing to the quality of the crystals and the presence of four bromo atoms in the molecules the *R* factor (0.058 for **2A** and 0.044 for **2B**) and the estimated standard deviations (see Table 3) are rather large. A detailed discussion of structural features is therefore inappropriate, but it is interesting to observe that the bromine-carbon lengths average 1.917 Å, the phenyl ring distances

Table 6. The distance from the center of the phenyl ring (C*) to the four bromine atoms of the diastereomers of **2**, calculated from the crystal structures of **2A** and **2B**.

Diastereomer	C*–Br(1) (Å)	C*–Br(2) (Å)	C*–Br(3) (Å)	C*–Br(4) (Å)
A	6.137	6.237	5.582	4.016
B	3.939	4.456	5.554	3.916

1.389 Å, and the bonds of phenyl attachment 1.507 Å, which compare very well with the corresponding averages in both 1,1-dibromo-2,3-diphenylcyclopropane¹⁷ and 1,1-dibromo-2-phenyl-2-(2-propenyl)cyclopropane.¹⁸ Furthermore, the two cyclopropane rings in both diastereoisomers show the bond asymmetry expected for phenyl-substituted and brominated cyclopropanes; thus, the C–C bond distal to the phenyl group is shortened relative to the mean value and the vicinal bonds are lengthened, whereas the bromine substituents seem to have little effect.^{18,19}

Finally, it is noteworthy that the distances between the phenyl group and the two CBr₂ moieties are significantly different in **2A**, but very similar in **2B** (Table 6). The shorter distance to the CBr₂ moieties are identical in **2B** (3.9 Å in both cases), but very different for **2A** (4.0 Å as compared with 6.1 Å).

Photolyses. Bromocyclopropanes **1**, **2A** and **2B**, which showed UV absorptions of intermediate intensity in the 258–265 nm region, were dissolved in a mixture of acetone and ethanol and irradiated through borosilicate (cut-off 265 nm). In order to facilitate a regiospecific reduction in each case overreduction should be avoided. Unfortunately, screening of available analytical methods revealed that the progress of the photolyses could only be assessed properly by ¹H NMR spectroscopy, which is rather unsuitable for continuous monitoring of the consumption of the starting material. This problem was solved, although not ideally, by irradiating several samples of each tetrabromide for a different length of time; the photolysates were then analyzed and those showing at least 95% conversion of the starting material were properly worked up and investigated thoroughly, particularly by NMR spectroscopy.

Photolysis of **1** following this protocol gave a product mixture which was essentially free of unreacted starting material as borne out by TLC analysis and by the ¹H NMR spectrum, which lacked a double doublet at 2.67 ppm (Fig. 2a). The spectrum of the crude product did, however, contain a complex collection of signals between 2.75 and 3.3 ppm, the region where the hydrogen atom on the bromo-substituted carbon atoms in both cyclopropane rings are expected to appear.^{8,9} The complexity of the signals clearly indicated that **1** had been converted into a mixture of isomeric tribromides, but in spite of extensive chromatographic experimentation pure samples of these products could not be isolated. Mixtures of tribromides were, however, obtained, and from their ¹H NMR spectra, shown in Figs. 2b–2d, it is evident that debromination of both *gem*-dibromo moieties has taken place. Fraction I gave rise to a double doublet, centered at 3.22 ppm, and a multiplet in the CHBr region of the spectrum (Fig. 2b) and therefore contained a mixture of the *cis* or *trans* isomer of 2,2',2'-tribromo-1-phenylbicyclopropyl (**3**), and 2,2,2'-tribromo-1-phenylbicyclopropyl (**4**). Fraction II, on the other hand, showed mainly a double doublet at 3.05 ppm in the CHBr region

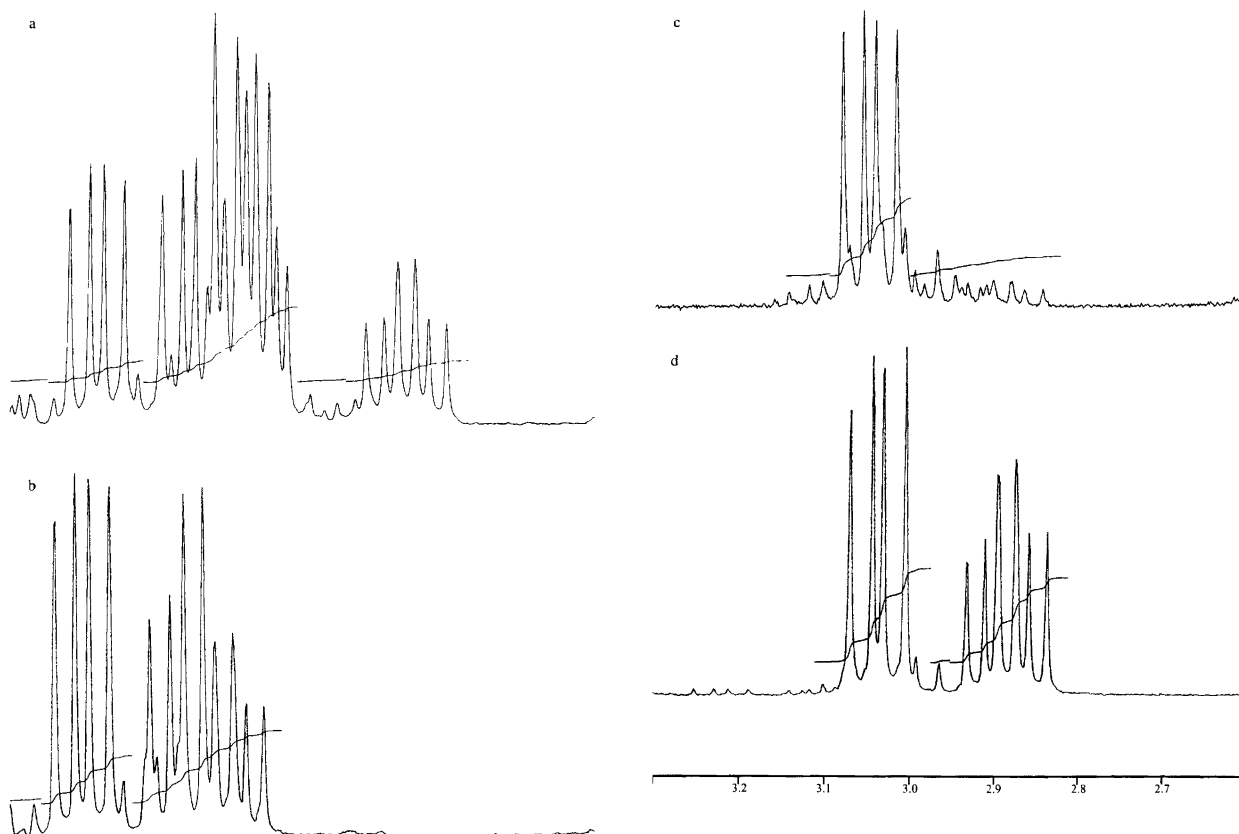
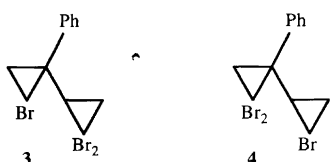


Fig. 2. The 2.60–3.30 ppm region of the 200 MHz ^1H NMR spectra of the tribromides formed by irradiation of 2,2,2',2'-tetrabromo-1-phenylbicyclopropyl (**1**): (a) the crude product; (b), (c) and (d) different fractions collected by flash chromatography.



(Fig. 2c) and consisted, therefore, predominantly of the isomer of **3** with a stereochemistry the opposite of that of the isomer of **3** present in fraction I. Finally, fraction III contained approximately equal amounts of the stereoisomer of **3** present in fraction II as well as the stereoisomer of **4** with a stereochemistry the opposite of that of the isomer of **4** present in fraction I; the latter compound gives rise to a multiplet centered at 2.88 ppm (Fig. 2a). Consequently, it is evident that photodebromination of **1** occurs at both rings. In keeping with a radical reaction all four stereoisomers were obtained, but owing to extensive signal overlap their relative ratio could not be determined accurately, although an estimate based on appropriate peaks and integrals in the NMR spectrum of the crude product (Fig. 2a) suggested that the four isomers are formed in roughly equal amounts.

When the diastereoisomers of **2** were irradiated separately as described above the regioselectivity turned out to be isomer-dependent. The ^1H NMR spectrum of the

crude product mixture from both **2A** and **2B** contained a number of overlapping signals of variable strength in the 2.95–3.30 ppm region where the hydrogen atom belonging to the CHBr moiety of the cyclopropane rings appears, and this clearly indicated that both compounds afforded mixtures of isomeric tribromides. However, the complexity of the mixtures was different as suggested by the signals in this region (Fig. 3). In neither case could a pure sample of any tribromide be obtained; fractionation by flash chromatography only furnished mixtures of isomeric tribromides with variable composition. When these mixtures were analyzed by ^1H NMR spectroscopy the double doublets associated with the CHBr moiety belonging to the phenylated cyclopropane ring were determined with certainty. From the peaks due to these double doublets, indicated with an asterisk in Fig. 3, it is evident that the tribromide mixture obtained from **2A** consisted predominantly of the *cis* and *trans* isomers of 1-bromo-2-(2,2-dibromocyclopropylmethyl)-2-phenylcyclopropane (**5**). The ratio of **5** to its regioisomer, 1,1-dibromo-2-(2-bromocyclopropylmethyl)-2-phenylcyclopropane (**6**), could not be determined accurately, but from Fig. 3a a 3:1 ratio seems to be roughly correct. The tribromide mixture from **2B**, on the other hand, contained relatively much more of **6**, the multiplets caused by the CHBr moiety of its *cis/trans* isomers

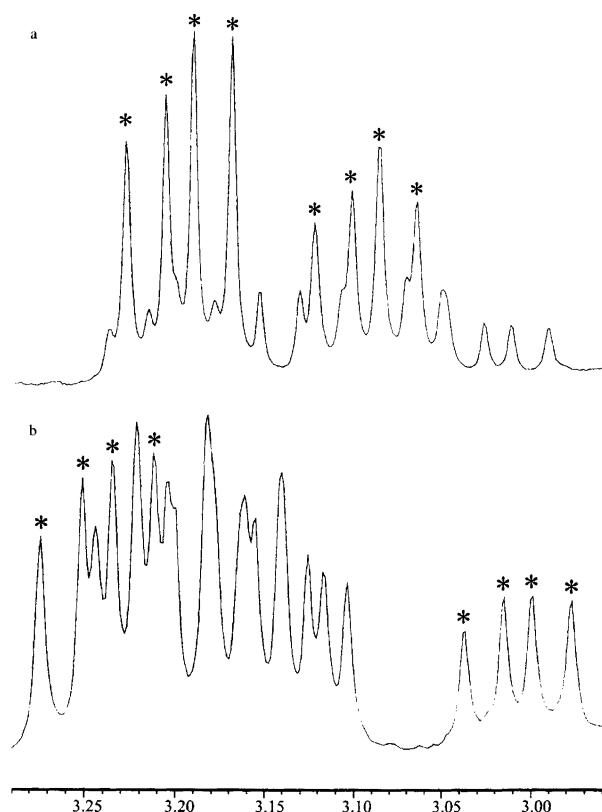
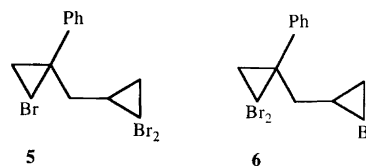


Fig. 3. The 2.96–3.29 ppm region of the 200 MHz ^1H NMR spectra of the tribromides formed by irradiation of 1,1-dibromo-2-(2,2-dibromocyclopropylmethyl)-2-phenylcyclopropane (**2**): (a) the crude product of diastereomer **2A**; (b) the crude product of diastereomer **2B**.

amounted to approximately half of the peak intensity in the CHBr region. Consequently, the photodebromination of **2A** is much more regioselective, with predominant attack on the phenylated ring, than in the case of **2B**, which reacts with no apparent selectivity.



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