

Short Communication

Photochemical Reduction of *gem*-Dihalocyclopropanes. II.† Proof of Formation of a Cyclopropyl Radical During Irradiation of 1,1-Dibromo-2-phenylcyclopropanes

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When phenyl-substituted *gem*-dibromocyclopropanes, dissolved in ethanol or a mixture of ethanol and acetone (added as sensitizer), are irradiated with Pyrex-filtered light ($\lambda > 295$ nm) the corresponding monobromides are obtained in moderate to excellent yields.¹ The monobromides are formed as mixtures of the *cis* and *trans* isomers with a *cis/trans* ratio similar to that observed when the same reductions are performed with tributyltin hydride (BTH). Since it is well established that reductive dehalogenation of halocyclopropanes with BTH involves cyclopropyl radicals^{2–5} and that excited *gem*-dibromo moieties can, in principle, form radicals,⁶ it was assumed that photoreduction of the title compounds also occurred via cyclopropyl radicals. However, an excited *gem*-dibromo moiety can also form carbocation and carbene intermediates,⁶ and it was therefore of interest to prove experimentally that radical intermediates are involved in the photochemical reduction of the title compounds.

Radicals with sufficiently long lifetimes can be detected by EPR spectroscopy, and several 1,1-dibromo-2-phenylcyclopropanes were dissolved in various solvents and irradiated in an EPR probe during spectra recording. However, no signals were detected and it was therefore decided to prepare a compound that allowed intramolecular trapping of any cyclopropyl radical formed during the photolysis. On the basis of several reports, showing that a cyclopropyl radical can be trapped by a 3-butenyl substituent attached to C-2,^{4,5} and an assessment of potential starting materials, 1-(2,2-dibromo-1-phenylcyclopropyl)-3-buten-1-ol (**1**) was selected as the cyclopropane of choice.

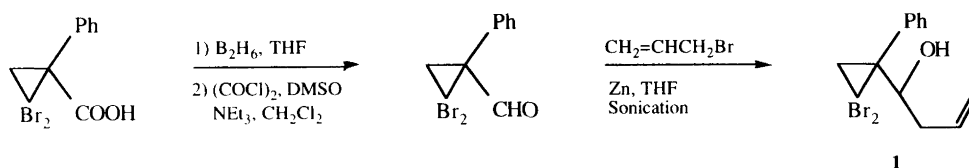
Cyclopropane **1** was easily synthesized in three steps

† Part I, see Ref. 1.

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from 2,2-dibromo-1-phenylcyclopropanecarboxylic acid (Scheme 1) and was obtained as a 10:1 mixture of diastereoisomers, which could not be separated chromatographically on a preparative scale. The yields in the first two steps were excellent (90%), but the third step furnished **1** in only 72% yield. With the aim of improving the yield, allylzinc bromide was replaced by the corresponding Grignard reagent in the last step, but this change led to no success; on the contrary, at least eight products were formed and **1** could not be isolated at all.

Irradiation of **1** dissolved in a mixture of ethanol and acetone afforded essentially two volatile compounds and several polar by-products as judged from GC and TLC analyses. The IR and NMR spectra of the reaction mixture lacked signals due to both allyl ethers and allenes, which are possible products if cyclopropyl cations^{7–9} and cyclopropylidene^{10–12} intermediates were formed. The volatile products were isolated by flash chromatography as a mixture in 48% total yield, but the two compounds could not be separated on a preparative scale. Spectroscopic and mass spectrometric investigations proved that the isolated products were diastereomers of 5-bromo-4-methyl-1-phenylbicyclo[3.1.0]hexan-2-ol (**2**) (see the Experimental section). The diastereomeric nature of the products was supported, in particular, by the ¹³C NMR spectrum of the mixture, which exhibited two sets of signals with small differences between most of the corresponding peaks. These observations are compatible with the formation of a cyclopropyl radical (**3**) during the photolysis of **1**, a radical which attacks the 3-butenyl substituent in an *exo-trig* fashion in accordance with Baldwin's rules,¹³ the work of Descoins *et al.*,⁵ and the fate of a large number of other radicals.^{14,15} The formation of **2**, therefore, supports the conclusion that



Scheme 1.

photochemical conversion of 1,1-dibromo-2-phenylcyclopropanes into 1-bromo-2-phenylcyclopropanes involves the corresponding 1-bromo-2-phenylcyclopropyl radicals (Scheme 2).

Bicyclohexanol **2** was also obtained when **1** was treated with BTH in diethyl ether at room temperature, but in addition 1-(2-bromo-1-phenylcyclopropyl)-3-buten-1-ol (**4**) was formed as borne out by a double doublet centered at 3.16 ppm in the ^1H NMR spectrum of the crude product. However, the lack of any such signal in the relevant region^{1,4} in the ^1H NMR spectrum of the photolysate from **1** proved that **4** was not formed during the photolysis of this dibromide. Therefore, the intramolecular trapping of the cyclopropyl radical **3** is relatively more efficient when the reduction is performed photochemically under our experimental conditions than with BTH, in spite of the fact that photochemically generated cyclopropyl radicals are known to abstract hydrogen effectively from ethanol.¹

Experimental

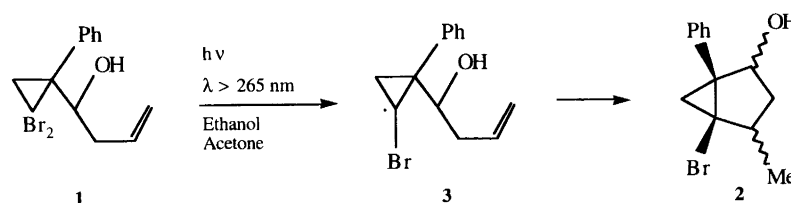
General. UV spectra were obtained on a Varian Cary 3 UV-VIS spectrophotometer. IR spectra were recorded on a Perkin-Elmer 1310 infrared spectrophotometer. NMR spectra were run on a Bruker Spectrospin AC 200 F spectrometer, at 200 MHz for ^1H and 50 MHz for ^{13}C , with tetramethylsilane (TMS) as an internal reference. Chemical shifts are reported in ppm downfield from TMS. 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. Mass spectra were obtained on a VG 7070H Micromass spectrometer operated in the EI mode at 70 eV. The spectra are reported as m/z (% rel. int.).

Acetone was dried with CaCl_2 and subsequently distilled. Diethyl ether was dried with sodium wire whereas THF was distilled from sodium-benzophenone. Absolute ethanol was used without further purification. Tributyltin hydride was prepared according to Kuivila.²

1-(2,2-Dibromo-1-phenylcyclopropyl)-3-buten-1-ol (**1**) was prepared in three steps from 2,2-dibromo-1-phenylcyclopropanecarboxylic acid.¹⁶

A solution of borane in tetrahydrofuran (0.85 M, 34 ml, 29 mmol) was added dropwise at room temperature to a stirred solution of 2,2-dibromo-1-phenylcyclopropanecarboxylic acid (7.7 g, 24 mmol) in tetrahydrofuran (10 ml) kept under nitrogen. The mixture was subsequently heated to 55 °C and stirred at this temperature for 3.5 h. Water and 10% aqueous sodium hydroxide were added, and the resulting mixture was extracted with diethyl ether. The combined organic fractions were washed with 6 M hydrochloric acid and dried (MgSO_4). Filtration followed by evaporation of the solvent gave 6.6 g (90%) of (2,2-dibromo-1-phenylcyclopropyl)methanol as a white solid, m.p. 48 °C (lit.¹⁷ 52.5 °C). The spectroscopic data were in accordance with the literature.¹⁸

2,2-Dibromo-1-phenylcyclopropanecarbaldehyde was prepared by Swern oxidation of (2,2-dibromo-1-phenylcyclopropyl)methanol. Oxalyl chloride (2.0 ml, 2.95 g, 23 mmol) was transferred to a round-bottom flask under nitrogen and diluted with dichloromethane (54 ml). The temperature was lowered to -60 °C and DMSO (3.69 ml, 4.06 g, 52 mmol) in dichloromethane (11 ml) was added dropwise over 5 min. Stirring was continued for 10 min at -60 °C after which a solution of (2,2-dibromo-1-phenylcyclopropyl)methanol (6.64 g, 22 mmol) in dichloromethane (22 ml) was added over 5 min at this temperature. The resulting mixture was stirred for 15 min before triethylamine (15.24 ml, 11.06 g, 109 mmol) was added dropwise. The cooling bath was removed and the stirred mixture was allowed to reach room temperature before water (60 ml) was added. After being stirred for an additional 30 min the mixture was extracted with dichloromethane. The combined organic extracts were washed with 8% hydrochloric acid, water, 10% aqueous sodium hydrogencarbonate, and water before being dried (MgSO_4). Filtration and evaporation of the solvent gave 6.0 g (91%) of essentially pure 2,2-dibromo-1-phenylcyclopropanecarbaldehyde as a



Scheme 2.

slightly yellow liquid. IR and ^1H NMR data were in accordance with the literature.¹⁹ ^{13}C NMR (CDCl_3): δ 28.5 (C), 30.6 (CH_2), 47.5 (C), 128.4 (CH), 128.5 (2 CH), 130.0 (2 CH), 133.9 (C), 194.6 (C=O).

Compound **1** was obtained by treating 2,2-dibromo-1-phenylcyclopropanecarbaldehyde with allylzinc bromide. Activated zinc²⁰ (3.1 g, 47 mmol) and dry THF (15 ml) were transferred to a reaction flask, which was immersed in an ultrasound bath containing ice-water. After sonication for 4 h under these conditions the aldehyde (5.7 g, 19 mmol), dissolved in dry THF (10 ml), was added quickly. The reaction mixture was then stirred at 30 °C for 2 h before 5% hydrochloric acid (100 ml) was added. The product was extracted with ether and the combined extracts were washed with 5% aq sodium carbonate and dried (MgSO_4). Filtration and evaporation of the ether gave 6.3 g of a brown, viscous residue, which was dissolved in hexane (75 ml) and mixed with active carbon. This mixture was refluxed for 10 min and filtered. After 3 days in the freezer, the product precipitated as white crystals, 4.7 g (72%), m.p. 71–72 °C. IR (CCl_4): 3570 (m), 3560–3150 (m), 1630 (m), 1490 (m), 1440 (m), 1420 (m), 1370 (m), 1280 (m), 1225 (m), 1090 (m), 1060 (s), 1040 (s), 1020 (s), 980 (m), 910 (s), 690 (s) cm^{-1} . ^1H NMR (CDCl_3): δ 1.75–2.15 (4 H, m including an AB system, A at 1.81 and B at 2.03, J 6.5 Hz), 2.25 (1 H, s), 3.67 and 3.77 (1 H, 2 dd in a ratio of 1:10, J 10.4 and 2.2 Hz and J 8.7 and 4.7 Hz, respectively), 4.75–5.10 (2 H, m), 5.55–6.90 (1 H, m), 6.95 and 7.33 and 7.70 (5 H, 3 br s, coalesced to 1 br s at 7.25 upon heating to 60 °C). ^{13}C NMR (CCl_4 , predominant diastereomer): δ 32.5, 34.0, 39.5, 43.1, 78.1, 117.7 (2 CH), 127.8 (2 CH), 127.9 (CH), 131.4 (C), 134.3 (CH_2), 135.8 (CH). ^{13}C NMR (CCl_4 , minor diastereomer): δ 31.8, 34.3, 39.4, 42.6, 77.2, 117.9 (2 CH), 127.9 (CH), 129.4 (CH, br, temperature-sensitive), 130.2 (C), 132.0 (CH, br, temperature-sensitive), 134.3 (CH_2), 135.9 (CH). UV (96% ethanol, λ_{max} , ϵ): 230 (1085), 256 (480), 262 (310) nm.

Irradiation of 1. A solution of **1** (0.40 g, 1.16 mmol) in a mixture of ethanol (100 ml) and acetone (20 ml) kept under nitrogen was irradiated with light from a 125 W medium-pressure mercury lamp. The lamp was kept in a water-cooled borosilicate well (cut-off 265 nm). The irradiation was stopped after 2 h, the solvents were evaporated off, and the residue was analyzed by TLC. Purification by flash chromatography (silica gel 230–400 mesh, hexane–ethyl acetate 70:30) gave 0.15 g (48%) of 5-bromo-4-methyl-1-phenylbicyclo[3.1.0]hexan-2-ol (**2**) as an oily 1:9 mixture of diastereomers. IR (film): 3700–3100 (br, m), 1590 (m), 1478 (m), 1438 (m), 1368 (m), 1295 (m), 1235 (m), 1162 (m), 1108 (m), 1065 (s),

1030 (s), 895 (m), 782 (m), 760 (s), 697 (s). ^1H NMR (CDCl_3): δ 0.60–0.92 (1 H, m), 1.05–1.65 (2 H, m), 1.10 (3 H, d, J 6.5 Hz), 1.75–2.00 (1 H, m), 2.27 (1 H, br s), 2.30–2.60 (1 H, m), 4.15–4.40 (1 H, m), 7.12–7.35 (5 H, m). ^{13}C NMR (CCl_4 , the predominant diastereomer): δ 15.6, 16.6, 37.0, 41.3, 43.3, 48.2, 76.9, 126.9 (CH), 128.0 (2 CH), 129.8 (2 CH), 138.9 (C). ^{13}C NMR (CCl_4 , the minor diastereomer): δ 20.9, 22.4, 36.2, 39.3, 43.1, 47.6, 76.1, 126.9 (CH), 128.1 (2 CH), 129.9 (2 CH), 138.5 (C). MS (isomeric mixture): 268 (M^+ , 0.2), 266 (M^+ , 0.2), 251 (3), 249 (2), 222 (8), 187 (100), 169 (30), 143 (60), 133 (21), 129 (16), 128 (27), 121 (23), 119 (73), 117 (42), 105 (42), 91 (36). Mol. wt.: calc. for $\text{C}_{13}\text{H}_{15}\text{BrO}$ 266.03062; found 266.02680.

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