  Bull. Chem. Soc. Jpn., 56, 1705—1709 (1983)

Photoaddition Reaction of 1,4-Dibromo-2,5-piperazinedione with Cyclohexene

Kuniaki Itoh

Department of Science of Material Reactions, Division of Science of Materials, Graduate School of Science and Technology, Kobe University, Kobe 657

(Received December 27, 1982)

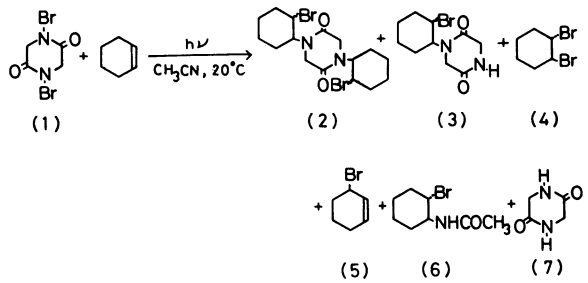
The photo-induced addition reaction of 1,4-dibromo-2,5-piperazinedione (1) with cyclohexene in acetonitrile gave 1 : 1-adducts[1-(2-bromocyclohexyl)-2,5-piperazinediones] and 1 : 2-adducts[1,4-bis(2-bromocyclohexyl)-2,5-piperazinediones] besides 3-bromocyclohexene, 1,2-dibromocyclohexane, and a solvent-incorporated product, *trans*-2-acetylamino-2-bromocyclohexane. Stereochemistry of the adducts was elucidated and mechanism of the addition reaction was discussed.

The characteristic feature of the reactions of *N*-halo imides and amides is their use in well-known allylic halogenation of olefins.[1,2] However, in some instances, the *N*-centered free radicals produced from *N*-halo imides or amides underwent addition to the olefinic double bonds to give addition products.[3-6] The two processes proceed competitively, but the one process can predominate over the other according to the subtle change in the reaction conditions. Thus, Skell and his co-workers[3,7] demonstrated that the photoreaction of *N*-chlorosuccinimide with cyclohexene gave *N*-(2-chlorocyclohexyl)succinimide, 3-chlorocyclohexene, and 4-chlorocyclohexene: the addition and the substitution being closely competitive processes. Chow and his co-workers[4] also showed that the substitution/addition ratio of the photoreaction of *N*-bromosuccinimide (NBS) with cyclohexene was dependent on temperature, solvents, added ethylene oxide (a hydrogen bromide trap), and molar ratio of reactants. The solubility of NBS in organic solvents changed noticeably the reaction pattern (hydrogen abstraction *vs.* addition to double bond) of NBS. Recently, we reported that irradiation of 1,4-dibromo-2,5-piperazinedione (**1**) with cyclohexene in the presence of alcohols efficiently induced alkoxy-bromination of cyclohexene in dichloromethane.[8] A free radical scavenger was employed to avoid possible free radical reactions. However, with less reactive alcohols, especially with *t*-butyl alcohol, the reaction gave an addition product, 1,4-dibromo-2,5-piperazinedione-cyclohexene 1 : 2-adduct, in addition to the expected alkoxybrominated product. Because the *N*-bromo compound (**1**) is almost insoluble in dichloromethane, the photoreaction had been carried out under heterogeneous conditions. The present investigation concerns the photoaddition reaction of **1** with cyclohexene in acetonitrile or halogenated hydrocarbon solvents. Acetonitrile is a poor solvent for **1**, but better than carbon tetrachloride. Structure of the adducts and the stereochemical course of the reaction are discussed.

Results and Discussion

The photoreaction of 1,4-dibromo-2,5-piperazinedione (**1**) was carried out with cyclohexene in a 1 : 10 mole ratio for 3 h at 20 °C in acetonitrile. The reaction mixture was vigorously stirred during the irradiation. After usual work-up, products were separated by silica gel chromatography. The results are given in Table 1.

The photoreaction of NBS with cyclohexene in carbon tetrachloride (heterogeneous conditions) gave no NBS-olefin adduct. In contrast, that in acetonitrile (homogeneous conditions) was reported to yield *N*-(2-bromocyclohexyl)succinimide.[2,4] With 1,4-dibromo-2,5-piperazinedione (**1**), predominant formation of 3-bromo-



Scheme 1.

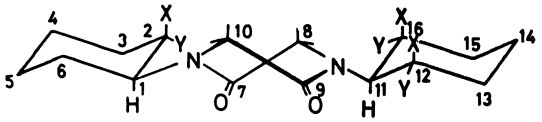
Table 1. Products of photoreaction of 1,4-dibromo-2,5-piperazinedione (**1**) with cyclohexene[a]

Solvent	Product yields/%											
	Total **2**	**2a**	**2b**	**2c**	**2d**	Total **3**	**3a**	**3b**	**4**[b]	**5**[b]	**6**	**7**
CH_3CN	34	15	7	10	2	18	13	5	17	24	1	36
CH_2Cl_2	38	17	7	12	2	7	5	2	15	35	0	45
$CHCl_3$	41	17	9	12	3	11	8	3	18	27	0	49
CCl_4	0					0			16	59	0	74[c]
CH_3CN[d]	7	4	1	2	0	0			26	9	0	92
CH_3CN[e]	25	11	5	7	2	12	8	4	17	14	3	39

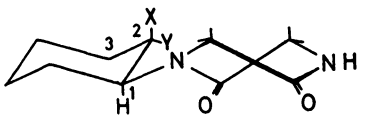
a) Irradiation of a mixture of **1** (20 mmol) and cyclohexene (200 mmol) in 100 ml of a solvent at 20 °C for 3 h. Isolated yields are given based on **1** employed. b) The yields are determined by GLC. c) Unchangel **1** was recovered in a 25% yield. d) Hydroquinone (0.1 molar equivalent to **1**) was added. e) The molar ratio of **1** to cyclohexene was 1/5.

cyclohexene (**5**) in a carbon tetrachloride solution (heterogeneous conditions) was observed. This implied the intervention of hydrogen abstraction at the allylic position of cyclohexene by means of the Goldfinger mechanism proposed originally for the reaction of NBS with olefins in carbon tetrachloride.[1] However, in better solvents for *N*-bromo imides and amides[9] (*e.g.* acetonitrile and dichloromethane; though the reaction conditions are still not completely homogeneous, they are somewhat more homogeneous than in the carbon tetrachloride solution) the addition of 2,5-dioxo-1-piperazinyl radical to the cyclohexene double bond proceeded rather smoothly to yield the adducts **2** and **3**. The 1,2-adducts, [1,4-bis(2-bromocyclohexyl)-2,5-piperazinedione, **2**], were separated by a silica-gel column to give four stereoisomers (**2a**, **b**, **c**, **d**) in a ratio given in Table 1. In addition, small amounts of the 1 : 1-adducts, [1-(2-bromocyclohexyl)-2,5-piperazinedione(**3**)], were isolated besides *trans*-1,2-dibromocyclohexane (**4**) and 3-bromocyclohexene (**5**). The 1 : 1-adducts were also separated to give a pair of stereoisomers (**3a**, **b**). Interestingly a small amount of a solvent-incorporated product, *trans*-2-acetylamino-2-bromocyclohexane (**6**), was obtained in case where acetonitrile was employed as the solvent. Other solvents gave no solvent-incorporated products. In all cases, 2,5-piperazinedione (**7**) was obtained in variable amounts.

Stereochemistry of the Adducts. The structures of all the products were determined by means of spectroscopic data and elemental analyses. The 1 : 1-adducts (**3a**, **b**) and 1 : 2-adducts (**2a**—**d**) showed characteristic infrared absorptions of the 2,5-piperazinedione moiety. The infrared absorption of these compounds (Table 2) allowed us to assign the adduct structures. Klaeboe, Lothe and Lunde[10] reported that, of the two C–Br stretching frequencies of bromocyclohexanes, the 685 cm^{-1} band should be assigned to the equatorial C–Br bond and the 658 cm^{-1} (lower frequency) band to the axial C–Br bond. In addition, *trans*-*N*-(2-chlorocyclohexyl)piperazine was reported to show its equatorial C–Cl stretching frequency at 730 cm^{-1}. The absorption of the axial C–Cl bond of the corresponding *cis* isomer was observed at 680 cm^{-1} (lower frequency).[5] The structures of the 1 : 1-adducts (**3a**, **b**) were confirmed to be 1-(2-bromocyclohexyl)-2,5-piperazinedione by means of preliminary spectroscopic analysis. In addition, from Table 2, it was deduced that **3a** has an equatorial bromine atom and **3b** has an axial bromine atom. Thus, **3a** and **3b** are possibly diastereoisomeric to each other. This assignment was reinforced by inspection of their NMR spectra. The axial –CHBr– protons of bromocyclohexane is known to appear at 3.82 ppm whereas the equatorial counterpart does at a lower field, 4.60 ppm. The half-height width of the former signal is wider than that of the latter. For example, Driguez and Lessard[5] reported that in *trans*-*N*-(2-chlorocyclohexyl)piperazine the axial proton on C_2 appeared at 3.72 ppm with a half-height width of 25 Hz, while in the *cis* isomer the equatorial proton on C_2 did at 4.43 ppm with a half-height width of 6.5 Hz. Chemical shifts and half-height widths given in Table 2 clearly



	2		12		16	
	X	Y	X	Y	X	Y
2a	H	Br	H	H	H	Br
2b	H	Br	H	Br	H	H
2c	H	Br	H	H	Br	H
2d	Br	H	H	H	Br	H



	X	Y
3a	H	Br
3b	Br	H

Scheme 2. The numbering of atoms is the same as in Fig. 1.

Table 2. IR and proton NMR spectral data for adducts

Compound	C–Br Stretching frequency/cm^{-1}		Chemical shifts (δ value) and half-height widths ($\Delta\nu_{1/2}$/Hz, given in parentheses)[a]						
	Equatorial	axial							
1 : 2-Adduct	C–Br	C–Br	H_1	H_2	H_{11}	H_{12}	H_{16}	H_8	H_{10}
2a	690	—	3.7—4.2 (18)	3.9—4.5 (17)	3.7—4.2 (18)	——	3.9—4.5 (17)	3.93[b]	3.93[b]
2b	680	—	3.7—4.2 (18)	4.0—4.6 (18)	3.7—4.2 (18)	4.0—4.6	—— (18)	3.92[b]	3.92[b]
2c	680	650	3.8—4.3 (18)	4.1—4.5 (16)	4.1—4.5 (16)	——	4.75—4.95 (7)	4.17[c] (J=17 Hz)	3.92[b]
2d	—	660	4.1—4.5 (18)	4.75—4.95 (7)	4.1—4.5 (18)	——	4.75—4.95 (7)	4.16[c] (J=16 Hz)	4.16[c] (J=16Hz)
1 : 1-Adduct									
3a	690	—	3.7—4.2 (18)	4.0—4.6 (18)	——	——	——	3.92[b]	4.00[b]
3b	—	655	4.1—4.6 (20)	4.7—4.9 (7)	——	——	——	4.13[c] (J=16 Hz)	3.97[b]

a) The numbering of atoms is the same as in scheme 2 and Fig. 1. b) Singlet. c) An AB-doublet centered at a given chemical shift position with a given J-value.

indicated the structure of **3a** as *trans*-1-(2-bromocyclohexyl)-2,5-piperazinedione, and that of **3b** as the corresponding *cis* isomer having an axial bromine substituent.

Structural elucidation of the 1 : 2-adducts (**2a**—**d**) was achieved taking the following consideration into account. The infrared absorptions of the 1 : 2-adducts showed that **2a** and **2b** have two equatorial bromine atoms, while **2c** has an axial and an equatorial bromine atoms. Interestingly, the presence of two axial bromine atoms in **2d** was indicated by its strong infrared absorption at 660 cm^{-1}. Each 1 : 2-adduct was reduced by tributyltin hydride to give identical 1,4-dicyclohexyl-2,5-piperazinedione. Accordingly these four 1 : 2-adducts were determined to be stereoisomeric to each other at the carbon atoms bound to bromine atoms. The chemical shifts and half-height widths of **2a** and **2b** (Table 2) indicated the presence of the *trans*-diaxial orientation of the vicinal protons (H_1/H_2, H_{11}/H_{12}, or H_{11}/H_{16}), which gave large half-height width absorptions, respectively. The 2,5-piperazinedione ring protons (H_8 and H_{10}) appeared as a singlet, indicating that they experienced an equivalent magnetic environment. A definitive structure assignment for **2a** was made by X-ray crystallography. A suitable single crystal of **2a** was obtained by careful recrystallization from acetone. The unit cell was found to be monoclinic, space group $P2_1/C$, with lattice parameters $a=13.37(1)$ Å, $b=11.59(1)$ Å, $c=11.93(1)$ Å, $\beta=98.55(7)°$, and $Z=4$. Of 4192 independent reflections obtained by using monochromated Mo *Ka* radiation, 1946 reflections with $|F_0|\geq 3\sigma(|F_0|)$ were considered to be observed.[11] The molecular structure of **2a** shown in Fig. 1 reveals that the C–Br bonds and the C=O groups are forced to located at an opposite direction by their dipole-dipole repulsion. The structure of **2b** was similarly determined as a diastereoisomer of **2a** as shown in Scheme 2 by its spectral characteristics.

The other 1 : 2-adducts, **2c** was found to possess an axial and an equatorial bromine substituents. The narrow half-height width observed for one of –CHBr– protons (an axial proton) supported this assignment. A crystal of **2c** obtained from methanol was monoclinic, space group C2/C, with lattice parameters $a=27.043$ (6) Å, $b=12.543(3)$ Å, $c=11.251(3)$ Å, $\beta=109.23(2)°$, and $Z=8$. The molecular structure of **2c** was determined by X-ray analysis, and shown by the ORTEP drawing in Fig. 1.[11] Crystallographic analysis gave the torsional angle of about 90° between the left-hand cyclohexane ring and the central 2,5-piperazinedione ring, and that of about 60° between the right-hand cyclohexane ring and the 2,5-piperazinedione ring. The central 2,5-piperazinedione ring was determined to exist in a flattened boat conformation. This molecular geometry resulted in characteristic NMR signals of **2c**. The structure of **2c** (Fig. 1 [C]) reveals that one of the protons on C_8 is placed close to the axial C_{16}–Br bond of the right-hand cyclohexane ring so that the C_8 methylene protons become magnetic nonequivalent to each other to give an AB quartet centered at 4.17 ppm. The other methylene proton on C_{10} appear at 3.92 ppm (singlet) as the corresponding C_8 and C_{10} protons of **2a** and **2b** do. The other chemical shift data and half hight widths are consistent with those expected from the depicted structure.

The structure of **2d**, which had two axial bromine atoms, was elucidated as shown in Scheme 2 taking the following spectral data into consideration; low field shift and narrow $\Delta\nu_{1/2}$ observed for both H_2 and H_{16}, and AB splitting of H_8 and H_{10} protons.

Course and Stereochemistry of Addition Reaction. The reaction did not occur in the dark. 1,4-Dibromo-2,5-piperazinedione (**1**) was hardly soluble in carbon tetrachloride, and the reaction gave no adducts, but the dominant allylic bromination was observed. The other chlorinated hydrocarbons showed a slightly enhanced solubility for **1**. The photoreaction of **1**

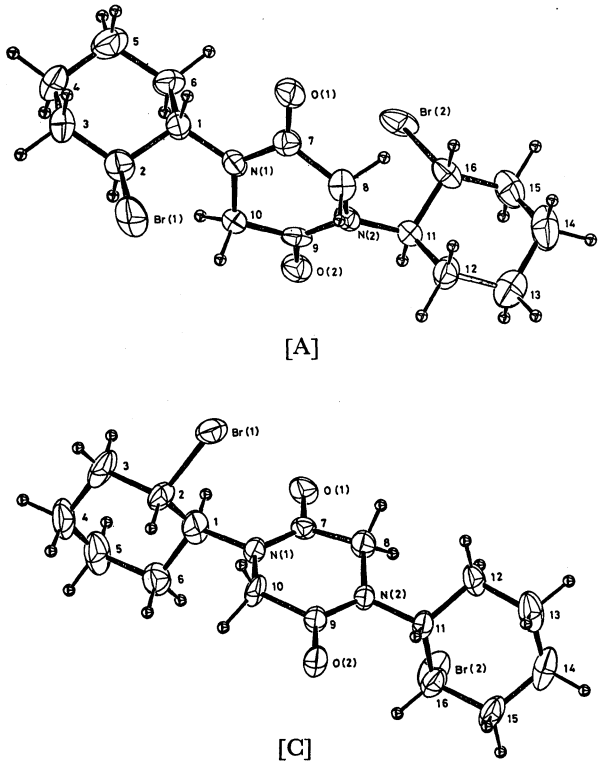
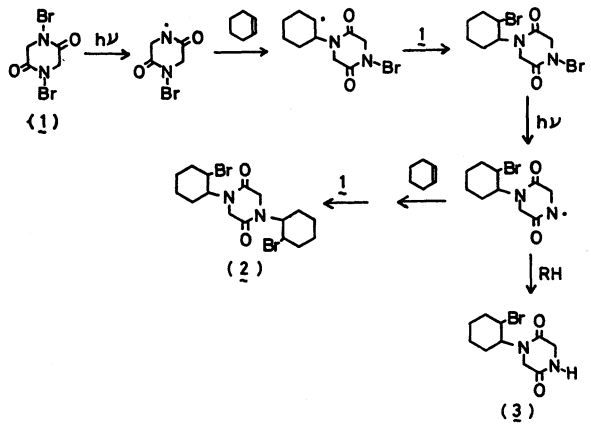


Fig. 1. ORTEP drawings of the 1 : 2-adducts. The numbering of atoms is the same as in Scheme 2.
[A]: **2a**, [C]: **2c**.

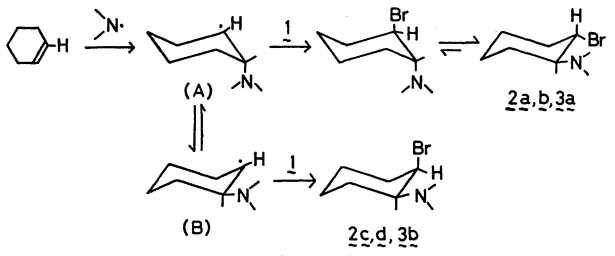


Scheme 3.

with cyclohexene in these solvents gave the adducts **2** and **3**. Acetonitrile was found to be the most convenient solvent for the photoreaction of **1**, although the solubility of **1** was not satisfactory. In acetonitrile the photoreaction of **1** with cyclohexene gave the adducts in considerable amounts. In the presence of hydroquinone, the yield of the adducts (**2** and **3**) decreases down to 7% from 52%. From this observation and the absence of rearranged products in the photoreaction of **1** with 3,3-dimethyl-1-butene,[12] an ionic reaction mechanism was ruled out. Thus the adducts were thought to be produced through a radical process involving the 2,5-dioxo-1-piperazinyl radical as the chain transfer species (Scheme 3).

In acetonitrile, a small amount of *trans*-2-acetylamino-2-bromocyclohexane (**6**) was produced. The yield of **6** was increased with an increased mole ratio of cyclohexene to **1**. The formation mechanism of **6** is to be noted. Photodecompotion of **2** in acetonitrile did not give rise to **6**. This suggests that **2** is not an intermediate to give **6**. Instead, the photoreaction of **1** with cyclohexene in acetonitrile-d_3 gave Me-d_3-**6**, indicating the intervention of a Ritter type reaction.[13] A concomitant reaction which is often encountered in NBS reactions is the ring opening to produce the isomeric 3-bromopropionyl isocyanate.[2] The reaction is reported to be enhanced in the presence of olefins.[14,15] However, in the present investigation, we could not detect any ring opening product.

It is reasonable to expect that the 2,5-dioxo-1-piperazinyl radical attacks the double bond of cyclohexene at the least hindered site, which corresponds to an axial direction in the resulting cyclohexyl radical (Scheme 4, A). The bromine atom is then transferred from **1** to this radical (*trans* addition), and following ring inversion give the adducts with equatorial bromine substituents (**2a**, **b**, and **3a**). The intermediate radical (A) can invert to give rise to the conformationally more favorable radical (B) having the equatorial 2,5-piperazinedione moiety. Inspection of the stereomodel of B indicates a sterically favored axial bromine attack which gives the adducts **2c**, **d**, and **3b**. Diastereomers **2a**, **b** having all substituents at the equatorial position of cyclohexane rings are undoubtedly most stable products, so that the yield of (**2a**+**2b**) is always exceeded that of (**2c**+**2d**). The conformationally unfavored adduct **2d** with two axial bromine substituents was produced in a lowest yield. In addition, it seems that highly symmetrical molecular geometry of **2a** (a center of symmetry, see Fig. 1) is responsible for its predominant formation over **2b**.



Scheme 4.

The regioselectivity of the addition of **1** to 1-methylcyclohexene and 3,3-dimethyl-1-butene provides a straightforward evidence for the 2,5-dioxo-1-piperazinyl radical as the initial attacking entity to the double bonds (Scheme 2).[12] As pointed out by Skell and Day[15] the radical generated by the processes like **1** + R $\cdot \rightarrow$ 2,5-dioxo-1-piperazinyl radical + R–Br has overwhelmingly σ_N–character (the first exited state). Recent ab initio[16] as well as INDO[17] calculations for the succinimido radical suggested that the ground state (π-radical) is 83 kJ mol^{-1} more stable than the first exited state (σ_N-radical). This energy difference nicely explains the selectivity differences observed for the hydrogen abstraction reactions by **1**, and the enhanced reactivity of the NBS σ_N-radical for aromatics.[2] For other cyclic imido and amido radicals, Apeloig and Schreiber[16] pointed out that the energy differences between the ground state π- and the first exited state σ_N-radical is expected to be greater than 83 kJ mol^{-1}. This difference may be responsible for the enhanced addition reactivity of the radical. However, absence of the radical isomerization and failure of the reaction of **1** with aromatics[12] indicate complex nature of 2,5-dioxo-1-piperazinyl radical.

Experimental

Cyclohexene was dried over Molecular Sieves 4A and distilled over copper(I) chloride prior to use. Acetonitrile was dried over calcium hydride and distilled. 1,4-Dibromo-2,5-piperazinedione (**1**) was prepared according to the procedure reported ealier.[8] IR spectra were recorded as KBr disk with JASCO IR-A-1 and IR-A-3 spectrometers. NMR spectra were measured on JEOL JNM-PMX-60 and JNM-PS-100 spectrometers using tetramethylsilane as the internal standard. Mass spectra were obtained by a Hitachi RMU-6MG spectrometer. GLC anaysis was carried out by a Yanagimoto Model G 1800-F. Irradiation was carried out using a Halos EHB–WU high pressure mercurry arc lamp (100 W).

Reaction of 1,4-dibromo-2,5-piperazinedione (1) with cyclohexene. A typical experimetal procedure is described. Irradiation of a mixture containing 5.44 g (20 mmol) of **1** and 16.43 g (200 mmol) of cyclohexene in acetonitrile (100 ml) was carried out under stirring for 3 h. The mixture was filtered to give 2,5-piperazinedione (**7**) in a 36% yield. A part of the filtrate was directly injected into a GLC column to determine the amounts of low boiling products: *trans*-1,2-dibromocyclohexane (**4**) and 3-bromocyclohexene (**5**) were produced in 17% and 24% yields, respectively. The rest of the filtrate was evaporated up to a syrup, which was separated by a column packed with silica gel using benzene–acetone (4 : 1) as a eluant. Yields are given in Table 1 on the basis of **1** employed. Physical constants of the isolated products are shown below. For characteristic IR absorptions and NMR chemical shifts, see Table 2.

1,4-Bis(2-bromocyclohexyl)-2,5-piperazinediones (2a): Mp 183—184 °C; IR, 1680, 1480, 1185 cm^{-1}; NMR($CDCl_3$), δ=1.1—2.7 (16H, m); MS (*m/e*), 438, 436, 434 (M^+), 357, 355, 275, 195, 115, 81. Found; C, 43.98, H, 5.76%; Calcd for $C_{16}H_{24}Br_2N_2O_2$; C, 44.06, H, 5.55%. **2b**: Mp 213—214 °C; IR, 1680, 1480, 1190 cm^{-1}; NMR($CDCl_3$), δ=1.1—2.6 (16H, m); MS (*m/e*), the same as that of **2a**. Found; C, 44.01, H, 5.93%; Calcd see above. **2c**: Mp 193.5—194.5 °C; IR, 1660, 1460, 1175 cm^{-1}; NMR($CDCl_3$), δ=1.1—2.7 (16H, m); MS (*m/e*), the same as that of **2a**. Found; C, 44.28, H, 5.80%; Calcd;

see above. **2d**: Mp 212—213 °C; IR, 1650, 1470, 1175 cm^{-1}, NMR($CDCl_3$), δ=1.1—2.6 (16H, m); MS (*m/e*), the same as that of **2a**. Found; C, 44.36, H, 5.71%; Calcd see above.

1-(2-Bromocyclohexyl)-2,5-piperazinedione (3a): Mp 165.5—166.5 °C; IR, 3300, 1680, 1470, 1190 cm^{-1}; NMR($CDCl_3$) δ=1.1—2.6 (8H, m), 7.10 (1H, s); MS (*m/e*), 274, 272 (M^+), 194, 115, 81. Found; C, 43.53, H, 5.94%; Calcd for $C_{10}H_{15}BrN_2O_2$; C, 43.65, H, 5.49%. **3b**: Mp 165—166 °C; IR, 3480, 1680, 1630, 1470, 1170 cm^{-1}; NMR($CDCl_3$), δ=1.1—2.5 (8H, m), 6.90 (1H, s); MS (*m/e*), the same as that of **3a**. Found; C, 43.29 H, 5.61%; Calcd see above.

trans-2-acetylamino-2-bromocyclohexane (6): Mp 116.5—117.5 °C (lit,[16] 109—110 °C). IR, 3300, 1620, 690 cm^{-1}; NMR($CDCl_3$), δ=1.1—2.6 (8H, m), 2.00 (3H, s), 3.8—4.1 (2H, m), 5.6—6.0 (1H, m); MS (*m/e*), 221, 219 (M^+), 140, 98, 81. Found; C, 43.62, H, 6.32%; Calcd for $C_8H_{14}BrNO$; C, 43.65, H, 6.41%.

Reduction of 1,4-Bis(2-bromocyclohexyl)-2,5-piperazinedione (2) with Tributyltin Hydride. Compound **2a** (73.5 mg, 0.17 mmol), tributyltin hydride (117 mg, 0.4 mmol), and AIBN (8 mg) were dissolved in 5 ml of benzene, and the mixture was kept in an atmosphere of nitrogen at 80 °C for 3 h. The solvent was evaporated off and the residure was chromatographed through a silica gel column using benzene–acetone (4 : 1) to give 1,4-dicyclohexyl-2,5-piperazinedione in a 85% yield; mp 230.5—232.0 °C; IR, 1650, 1480, 1180 cm^{-1}; NMR ($CDCl_3$), δ=0.9—2.2 (20H, m), 3.93 (4H, s), 3.9—4.6 (2H, m). Found; C, 68.80, H, 9.40%; Calcd for $C_{16}H_{26}N_2O_2$; C, 69.03, H, 9.41%. All the other isomer, **2b—d**, were reduced similarly, and the same 1,4-dicyclohexyl-2,5-piperazinedione was obtained in all cases.

The author is grateful to Professor Akira Sera, Faculty of Science, Kobe University for his comments and suggestions for improvement of the manuscript, and wishes to thank Professor Kazumi Nakatsu and Mr. Kohmei Kafuku, Faculty of Science, Kwansei Gakuin University, for X-ray crystallographic analysis.

References

1) J. S. Pizey, "Synthetic Reagents," Ellis Horword Ltd., Chichester (1974), Vol. II, Chap. 1.
2) P. S. Skell and J. C. Day, *Acc. Chem. Res.*, **11**, 381 (1978).
3) J. C. Day, M. K. Katsaros, W. D. Kocher, A. E. Scott, and P. S. Skell, *J. Am. Chem. Soc.*, **100**, 1950 (1978).
4) F.-L. Lu, Y.M.A. Naguib, M. Kitadani, and Y. L. Chow, *Can. J. Chem.*, **57**, 1967 (1979).
5) H. Driguez and J. Lessard, *Can. J. Chem.*, **55**, 720 (1977).
6) S. Wolfe and D. V. C. Awang, *Can. J. Chem.*, **49**, 1384 (1971).
7) J. C. Day, M. J. Lindstrom, and P. S. Skell, *J. Am. Chem. Soc.*, **96**, 5616 (1974).
8) A. Sera, H. Yamada, and K. Itoh, *Bull. Chem. Soc. Jpn.*, **53**, 219 (1980).
9) The use of carbon tetrachloride (solubility of 0.005 mol/l for NBS) in allylic bromination of olefins with NBS allows the bromine radical to be a chain carrier. In acetonitrile (solubility of 0.8 mol/l for NBS), the increased concentration of NBS changes the dominant chain carrier species from the bromine radical to the succinimido radical, so that double bond addition products can be obtained.[2]
10) P. Kaeboe, J. J. Lothe, and K. Lunde, *Acta Chem. Scand.*, **10**, 1465 (1956).
11) Details of the X-ray analysis will be reported elsewhere.
12) Unpublished results.
13) For a similar results, see Y. Wada and R. Oda, *Bull. Chem. Soc. Jpn.*, **43**, 2167 (1970).
14) R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 354, 3142 (1963).
15) P. S. Skell and J. C. Day, *J. Am. Chem. Soc.*, **100**, 1951 (1978).
16) Y. Apeloig and R. Schreiber, *J. Am. Chem. Soc.*, **102**, 6144 (1980).
17) T. Koenig and R. A. Wielsek, *Tetrahedron Lett.*, **1975**, 2007.