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Photoinduced Addition Reaction of 1,4-Dibromo-2,5-piperazinedione with 1-Alkenes

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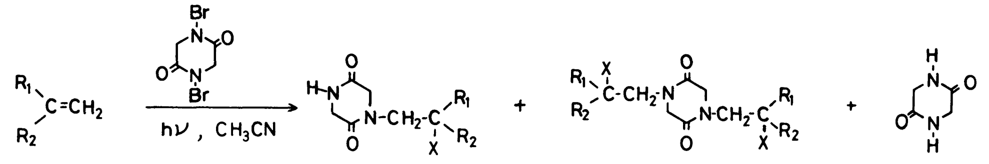
Irradiation of 1,4-dibromo-2,5-piperazinedione (**1**) with olefins in acetonitrile gave mixtures of addition products (1:1-adducts and 1:2-adducts). Addition of 1,2-epoxybutane (a hydrogen bromide scavenger) resulted in enhanced yields of the adducts. Structures of the adducts were elucidated and a reaction mechanism is discussed.

The allylic bromination of olefins by *N*-bromosuccinimide (NBS) was believed to involve the bromide atom chain (the Goldfinger mechanism). However, Skell and his co-workers[1,2] showed that the reaction of NBS with cyclohexene in dichloromethane gave 3- and 4-bromocyclohexenes and 1-bromo-2-succinimidocyclohexane. Thus the substitution and the addition are competitive processes (substitution/addition=0.17). Chow and his co-workers[3] similarly exemplified that in the photolysis of an acetonitrile solution of NBS in the presence of cyclohexene the succinimido radical preferentially added to the olefin double bond to give the same adduct. These findings suggest the intervention of the succinimido radical as the chain carrier where the concentration of NBS is kept high by using good NBS dissolving solvents and the concentration of the bromine molecule is kept low by added olefins. The addition reaction of acylaminyl radicals to olefins, however, has not been so thoroughly examined. Thouchard and Lessard[4] reported that the photochemical reaction of *N*-haloacetamides with olefins gave addition products in good yields, but *N*-halo-*N*-methylacetamides failed to add to simple olefins.[5] In a previous paper,[6] we described that irradiation of 1,4-dibromo-2,5-piperazinedione (**1**) with cyclohexene resulted in the radical addition of **1** to cyclohexene to give 1-(2-bromocyclohexyl)-2,5-piperazinediones (1:1-adducts) and 1,4-bis(2-bromocyclohexyl)-2,5-piperazinediones (1:2-adducts) in acetonitrile, dichloromethane, or chloroform, which are characterized as good solvents for **1**. This paper concerns the product distribution in photoaddition of **1** to 1-alkene isomers in acetonitrile. The structures of adducts and the reaction mechanism are also discussed.

Results and Discussion

The photoreaction of 1,4-dibromo-2,5-pipera-



	R_1	R_2		R_1	R_2	X		R_1	R_2	X
2	n-C_4H_9	H	**2′(OH)**	n-C_4H_9	H	OH	**2″a,b**	n-C_4H_9	H	Br
							2″(OH)a,b	n-C_4H_9	H	OH
3	n-C_3H_7	CH_3	**3′**	n-C_3H_7	CH_3	Br	**3″a,b**	n-C_3H_7	CH_3	Br
4	i-C_3H_7	CH_3	**4′**	i-C_3H_7	CH_3	Br	**4″a,b**	i-C_3H_7	CH_3	Br
5	t-C_4H_9	H	**5′**	t-C_4H_9	H	Br	**5″a,b**	t-C_4H_9	H	Br

Scheme 1.

Table 1. PRODUCT DISTRIBUTION OF PHOTOREACTION OF 1,4-DIBROMO-2,5-PIPERAZINEDIONE WITH 1-ALKENES[a)]

	Product distribution (yields/%)				
	1:1-Adduct		1:2-Adduct		2,5-Piperazinedione
1-Hexene(**2**)	**2′(OH)**	11	**2″a,b**	5[c)]	54
			2″(OH)	7[c)]	
1-Hexene(**2**)[b)]	**2′(OH)**	16	**2″a,b**	21[c)]	39
			2″(OH)a,b	9[c)]	
2-Methyl-1-petene(**3**)	**3′**	5	**3″a,b**	45[c)]	3
2,3-Dimethyl-1-butene(**4**)	**4′**	3	**4″a**	17	8
			4″b	11	
3,3-Dimethyl-1-butene(**5**)	**5′**	7	**5″a**	2	trace[d)]
			5″b	2	

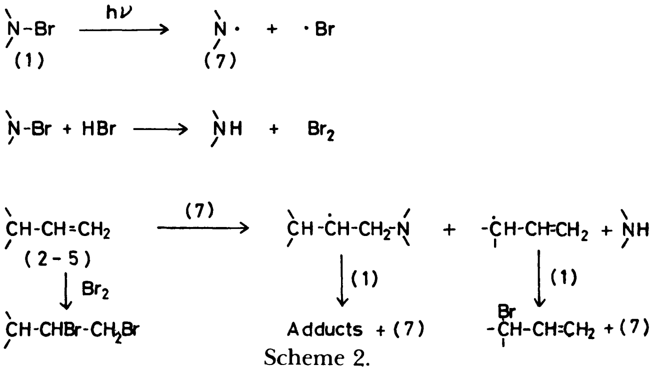
a) A mixture of **1** (2 mmol) and an olefin (20 mmol) in 10 cm^3 of acetonitrile was irradiated at ambient temperature for 5 h. Isolated yields are given based on **1** employed. b) 1,2-Epoxybutane (4 mmol) was added. c) A mixture of two stereoisomers. d) Unchanged **1** was recovered in 60% yield.

zinedione (**1**, 2 mmol) with isomeric 1-alkenes (**2**—**5**, 20 mmol) was carried out in acetonitrile using a high pressure mercury lamp at ambient temperature. The reaction gave mixtures of 1:1-adducts (**2′**—**5′**; characterized by ′) and 1:2-adducts (**2″**—**5″**; characterized by ″) in addition to allylic brominated products and dibromides. The adduct mixtures were separated by silica-gel column chromatography, and the structures were determined by elemental and spectroscopic analyses. The results are summarized in Scheme 1 and Table 1.

A chromatographic separation of the adduct mixtures obtained from the photoreaction of **1** with 1-hexene (**2**) gave an isomer mixture of bromine-containing 1:2-adducts (**2″**), an isomer mixture of hydroxyl group-containing 1:2-adducts (**2″**(**OH**)), and a hydroxyl group-containing 1:1-adduct (**2′**(**OH**)). No bromine-containing 1:1-adduct was obtained. Addition of 1,2-epoxybutane (a hydrogen bromide scavenger) resulted in increased yields of the adducts. The adduct mixture (**2″**) was re-chromatographed to give isomers **2″a** and **2″b**. Both **2″a** and **2″b** had two bromine atoms, and they gave similar NMR and IR spectra. Treatment of **2″a** and **2″b** by tributyltin hydride afforded identical 1,4-dihexyl-2,5-piperazinedione (**2″**(**H**)). NMR spectra of **2″a** and **2″b**, and their reduction product (**2″**(**H**)) indicated that the 2,5-dioxo-1-piperazinyl group added to the less substituted carbon atom of **2**, and that **2″a** and **2″b** are stereoisomers each other at the carbon atoms bearing bromine atoms. The hydroxyl group-containing adduct consisted of two isomers, **2″**(**OH**)**a** and **b** (in about a 3:4 ratio (NMR)); they hardly separated on TLC. IR spectra of **2″**(**OH**)**a**, **b** showed the presence of hydroxyl groups, and no bromine atom was contained as checked by MS; the distinct M^+-2H_2O was detected on MS spectra. The structure of **2′**(**OH**) was deduced by similar analysis.

The adduct mixtures obtained from the photoreactions of **1** with 2-methyl-1-pentene (**3**), 2,3-dimethyl-1-butene (**4**), and 3,3-dimethyl-1-butene (**5**) were also analyzed, and the structures of the corresponding 1:1-adducts (**3′**—**5′**) and 1:2-adducts (**3″**—**5″**) were similarly determined as given in Scheme 1. In these cases, adducts corresponding to **2′**(**OH**) and **2″**(**OH**) were not obtained.

For allylic brominations of alkenes with NBS, Goldfinger[7] pointed out that the bromine atom should be the hydrogen atom abstracting species of the chain sequence, and that the succinimido radical should be less reactive. However, evidence was reported that disclosed unexpected high reactivity of the succinimido radical in the addition reactions to olefinic double bonds.[1,3] We had also reported that the photoreaction of 1,4-dibromo-2,5-piperazinedione (**1**) with cyclohexene in acetonitrile gave a considerable amount of addition products.[6] The 1-alkenes employed in the present study gave similar adducts (Scheme 1 and Table 1). The respective bromine-containing 1:2-adduct consisted of two diasteromers. The 2,5-piperazinedione moieties were found to be attached to the less substituted carbon atoms of the original olefins. The direction of addition appears to be determined by the mode of addition of the 2,5-dioxo-1-piperazinyl radical (**7**) to the olefins to give more stable alkyl radicals. The stability of the intermediate alkyl radicals is responsible for the amounts of the adducts produced (tertiary alkyl radicals from **3** and **4**, while secondary alkyl radicals from **2** and **5**). In the photoreaction with **5**, no rearranged products such as 1-(3-bromo-2,3-dimethylbutyl)- or 1-(4-bromo-2,3-dimethyl-2-butyl)-2,5-piperazinedione were detected. This indicates that the addition proceeded through a radical mechanism. Steric inhibition to addition is also observed in the cases where methyl groups are present at the C_3 position of the olefins.



Scheme 2.

In the photoreaction of **1** with 1-hexene (**2**), 1-(2-hydroxyhexyl)-2,5-piperazinedione (**2′**(**OH**)) and a mixture of 1,4-bis(2-hydroxyhexyl)-2,5-piperazinediones (**2″**(**OH**)**a**, **b**) were produced as well as 1,4-bis(2-bromohexyl)-2,5-piperazinediones (**2″a**, **b**). Hydrolysis during chromatographic separation is considered to result in these hydroxyl group-containing adducts from corresponding bromine-containing adducts. Participation by the neighboring amide group may be responsible for facilitating the hydrolysis. Because of the bulk of the neighboring 2,5-piperazinedione moiety, this assisted hydrolysis works only in the case of the adducts produced from **2**. The presence of methyl substituents at the C_2 and/or C_3 positions of the side chains of **3″**, **4″**, and **5″** makes the *N*-participation impossible, so that no hydroxy group-containing adducts exist in the reactions with **3**, **4**, and **5**. A treatment of an acetone solution of **2″** with silica gel containing a small amount of hydrobromic acid actually yielded **2″**(**OH**). To trap hydrogen bromide generated during the photoreaction, the reaction was examined in the presence of 1,2-epoxybutane. The addition of two mole equivalents of 1,2-epoxybutane results in an increased yield of the adducts, and the ratio of **2″**(**OH**) to **2″** is considerably reduced. This implies that the hydrolysis of **2″** is catalyzed by hydrogen bromide.

Photoreaction of **1** with electron poor olefins (methyl acrylate, stilbene, *etc*) gave few adducts even in the presence of 1,2-epoxybutane, but a considerable amount of polymers and dibromides were produced.

Experimental

The olefins and 1,2-epoxybutane were dried over Molecular Sieve 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 earlier.[8] IR spectra (KBr) were recorded with JASCO IR-A-1 and -3 spectrometers. NMR spectra were measured on JEOL JNM-PMX-60 and

PS-100 spectrometers using tetramethylsilane as the internal standard. Mass spectra were obtained by a Hitachi RMU-6MG and ESCO EMD-05A spectrometers. Irradiation was conducted through a Pyrex filter using an Ushio Model UI-501e high-pressure mecury arc lamp (500 W).

*Reaction of 1,4-Dibromo-2,5-piperazinedione (**1**) with 1-Hexene (**2**) in the Presence of 1,2-Epoxybutane.* A typical experimental procedure is described. Irradiation of a mixture containing 544 mg (2 mmol) of **1**, 1.68 g (20 mmol) of 1-hexene and 1,2-epoxybutane (288 mg, 4 mmol) in acetonitrile (10 cm^3) was carried out with stirring at the ambient temperature for 4 h. The mixture was filtered to give 2,5-piperazinedione in a 39% yield. The filtrates (2—3 runs) were combined, and after removal of the solvent the products were separated on a silica-gel column (benzene→benzene and acetone→acetone). The 1:2-adducts **2″a,b** were rechromatographed on a silica-gel column (benzene→benzene and acetone) to give a pure specimen. Yields are given in Table 1 on the basis of **1** employed. Physical constants of the isolated products are shown below.

*1,4-Bis(2-bromohexyl)-2,5-piperazinedione (**2″a**)*: Mp 125—126 °C (from benzene). IR, 1670, 1490, 1430, 1340, 1250, 1190, and 950 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=0.9 (6H, m, CH$_3$), 1.0—2.0 (12H, m, -(CH$_2$)$_3$-), 3.1—3.8 (4H, m, N-CH$_2$-), 4.04 (2H, s, ring H), 4.12 (2H, s, ring H), and 4.2—4.5 (2H, m, -CHBr-).

Found: C, 43.43; H, 6.49%. Calcd for $C_{16}H_{28}Br_2N_2O_2$; C, 43.65; H, 6.14%.

2″b: Mp 92—93.5 °C (from benzene). IR, 1670, 1495, 1430, 1340, 1250, 1190, and 950 cm^{-1}. ^{1}H NMR(CDCl$_3$), δ=0.9 (6H, m, CH$_3$), 1.0—2.1 (12H, m, -(CH$_2$)$_3$-), 3.1—3.8 (4H, m, N-CH$_2$-), 4.08 (2H, s, ring H), 4.19 (2H, s, ring H), and 4.3—4.6 (2H, m, -CHBr-).

Found: C, 43.05; H, 6.58%. Calcd see above.

*1,4-Bis(2-hydroxyhexyl)-2,5-piperazinedione (**2″(OH)a,b**)*: A mixture of two isomers (*a*:*b*=3:4). Mp 213.5—215.0 °C (from ethanol-hexane). IR, 3400, 1650, 1510, 1425, 1345, and 1130 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=0.9 (6H, m, CH$_3$), 1.0—1.5 (12H, m, -(CH$_2$)$_3$-), 3.0—3.5 (4H, m, N-CH$_2$-), 3.5—3.9 (2H, m, -C$\underline{H}$(OH)-), 3.82 (2H, broad s, OH), and 4.01 (4H, s, ring H). MS (*m/z*), 278 (M$^+$−2H$_2$O), 223, 205, 145, 111, 84, and 56.

Found: C, 61.03; H, 9.83; N, 8.89%. Calcd for $C_{16}H_{30}N_2O_4$; C, 61.12; H, 9.62; N, 8.91%.

*1-(2-Hydroxyhexyl)-2,5-piperazinedione (**2′(OH)**)*: Mp 219—220 °C (from ethanol-hexane). IR, 3400, 3230, 1650, 1495, 1425, 1330, and 1130 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=0.9 (3H, m, CH$_3$), 1.1—1.6 (6H, m, -(CH$_2$)$_3$-), 2.9—3.5 (2H, m, N-CH$_2$-), 3.5—3.9 (1H, m, -C$\underline{H}$(OH)-), 3.72 (2H, s, ring H), 3.88 (2H, s, ring H), 4.25 (1H, broad s, OH), and 7.85 (1H, s, NH). MS (*m/z*), 214 (M$^+$), 196 (M$^+$−H$_2$O), 157, 128, 115, and 99.

Found: C, 56.05; H, 8.65; N, 13.46%. Calcd for $C_{10}H_{18}N_2O_3$: C, 56.05; H, 8.47; N, 13.07%.

*Hydrogenolysis of 1,4-Bis(2-bromohexyl)-2,5-piperazinedione (**2″a, b**) with Tributyltin Hydride.* The compound (**2″a** or **2″b**) (149 mg, 0.34 mmol), tributyltin hydride (24 mg, 0.82 mmol), and AIBN (16 mg) were dissolved in 5 cm^3 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 residue was chromatographed on a silica-gel column using benzene-acetone (4:1) to give 1,4-dihexyl-2,5-piperazinedione (**2″(H)**) in 95% yield: Mp 85—86 °C (from benzene). IR, 1660, 1495, and 1335 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=0.9 (6H, m, CH$_3$), 0.9—2.0 (16H, m, -(CH$_2$)$_4$-), 3.34 (4H, t, *J*=7 Hz, N-CH$_2$-), and 3.88 (4H, s, ring H).

Found: C, 68.18; H, 10.87%. Calcd for $C_{16}H_{30}N_2O_2$: C, 68.04; H, 10.71%.

*Photoadducts of 2-Methyl-1-pentene (**3**) with **1**.* *1,4-Bis(2-bromo-2-methylpentyl)-2,5-piperazinedione (**3″a, b**)*: A mixture of two isomers. Mp 111—113 °C (from benzene-hexane). IR, 1680, 1490, 1425, 1330, 1200, and 1190 cm^{-1}. ^{1}H NMR (C$_6$H$_6$), δ=0.9 (6H, m, CH$_3$), 1.2—2.1 (8H, m, -(CH$_2$)$_2$-), 1.70 (6H, s, -CBr(CH$_3$)-), 3.55—4.05 (4H, two AB quartets, *J*=14 and 16 Hz, N-CH$_2$-), and 4.10 (4H, s, ring H).

Found: C, 44.04; H, 6.67%. Calcd for $C_{16}H_{28}Br_2N_2O_2$: C, 43.65; H, 6.36%.

*1-(2-Bromo-2-methylpentyl)-2,5-piperazinedione (**3′**)*: Mp 91.5—93 °C (from benzene-hexane). IR, 3210, 1670, 1475, 1325, and 1115 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=0.97 (3H, m, CH$_3$), 1.2—2.0 (4H, m, -(CH$_2$)$_2$-), 1.68 (3H, s, CBr (CH$_3$)-), 3.53 and 3.91 (center) (2H, AB quartet, *J*=15 Hz, N-CH$_2$-), 3.93 (2H, s, ring H), 4.16 and 4.31 (center) (2H, AB quartet, *J*=17 Hz, ring H), and 7.62 (1H, s, NH).

Found: C, 43.20; H, 6.15%. Calcd for $C_{10}H_{17}BrN_2O_2$: C, 43.33; H, 6.18%.

*1,4-Bis(2-methylpentyl)-2,5-piperazinedione (**3″(H)**)*: Mp 88—89 °C (from hexane). IR, 1660, 1480, 1325, 1285, and 1190 cm^{-1}; ^{1}H NMR (CDCl$_3$), δ=0.9 (6H, m, CH$_3$), 0.94 (6H, s, CH(C$\underline{H}_3$)-), 1.0—1.9 (10H, m, -(CH$_2$)$_2$-CH-), 3.24 and 3.85 (center) (4H, AB quartet, *J*=7 Hz, N-CH$_2$-), and 3.92 (4H, s, ring H).

Found: C, 67.75; H, 10.61%. Calcd for $C_{16}H_{30}N_2O_2$: C, 68.04; H, 10.71%.

*1-(2-Methylpentyl)-2,5-piperazinedione (**3′(H)**)*: Mp 121.5—123.0 °C (from hexane). IR, 3200, 1670, 1475, 1335, 1280, and 1015 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=0.9 (3H, m, CH$_3$), 0.93 (3H, s, -CH(C$\underline{H}_3$)-), 1.0—1.9 (5H, m, -(CH$_2$)$_2$-CH-), 3.21 and 3.83 (center) (2H, AB quartet, *J*=7 Hz, N-CH$_2$-), 3.95 (4H, s, ring H), and 7.48 (1H, s, NH).

Found: C, 60.61; H, 8.90%. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15%.

*Photoadducts of 2,3-Dimethyl-1-butene (**4**) with **1**.* *1,4-Bis(2-bromo-2,3-dimethylbutyl)-2,5-piperazinedione (**4″a**)*: Mp 104—105 °C (from benzene). IR, 1680, 1480, 1380, 1320, 1205, 1180, and 1030 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=1.10 (12H, d, *J*=6 Hz, CH(C$\underline{H}_3$)$_2$), 1.65 (6H, s, CBr(CH$_3$)-), 1.5—2.2 (2H, m, -C$\underline{H}$(CH$_3$)$_2$), 3.38 and 4.22 (center) (4H, AB quartet, *J*=15 Hz, N-CH$_2$-), and 4.10 and 4.58 (center) (4H, AB quartet, *J*=16 Hz, ring H).

Found: C, 43.67; H, 6.54%. Calcd for $C_{16}H_{28}Br_2N_2O_2$: C, 43.65; H, 6.36%.

4″b: Mp 109—110 °C (from benzene). IR, 1670, 1490, 1380, 1325, 1180, and 1030 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=1.12 (12H, d, *J*=6 Hz, CH(C$\underline{H}_3$)$_2$), 1.67 (6H, s, CBr(CH$_3$)-), 1.5—2.2 (2H, m, C$\underline{H}$(CH$_3$)$_2$), 3.26 and 4.23 (center) (4H, AB quartet, *J*=15 Hz, N-CH$_2$-), and 4.02 and 4.74 (center) (4H, AB quartet, *J*=17 Hz, ring H).

Found: C, 43.72; H, 6.37%. Calcd above see.

*1-(2-Bromo-2,3-dimethylbutyl)-2,5-piperazinedione (**4′**)*: Mp 210 °C (dec.) (from benzene). IR, 3320, 3210, 1670, 1655, 1470, 1320, 1105, and 1020 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=1.08 (6H, d, *J*=6 Hz, -CH(C$\underline{H}_3$)$_2$), 1.66 (3H, s, -CBr(CH$_3$)-), 1.5—2.2 (1H, m, -C$\underline{H}$(CH$_3$)$_2$), 3.28 and 4.26 (center) (2H, AB quartet, *J*=15 Hz, N-CH$_2$-), 3.98 (2H, s, ring H), 3.99 and 4.61 (center) (2H, AB quartet, *J*=17 Hz, ring H), and 7.69 (1H, s, NH).

Found: C, 43.04; H, 6.18%. Calcd for $C_{10}H_{17}BrN_2O_2$: C, 43.33; H, 6.18%.

*1,4-Bis(2,3-dimethylbutyl)-2,5-piperazinedione (**4″(H)**)*: Mp 70—72 °C (from benzene-hexane). IR, 1670, 1480, 1335, and 1180 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=0.87 (12H, m, CH(C$\underline{H}_3$)$_2$), 1.3—2.0 (4H, m, -C$\underline{H}$(CH$_3$)-C$\underline{H}$(CH$_3$)$_2$), 1.66 (6H, d, *J*=9 Hz, CH(C$\underline{H}_3$)-), 3.2—3.8 (4H, m, N-CH$_2$-), 3.88 (2H, s, ring H), and 4.07 (2H, s, ring H).

Found: C, 67.99; H, 10.26%. Calcd for $C_{16}H_{30}N_2O_2$: C, 68.04; H, 10.71%.

*1-(2,3-Dimethylbutyl)-2,5-piperazinedione (**4′(H)**)*: Mp 163—165 °C (from benzene-hexane). IR, 3220, 1670, 1470, 1320, and 1110 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=0.87 (6H, m, CH-(C$\underline{H}_3$)$_2$), 1.3—2.1 (2H, m, -C$\underline{H}$(CH$_3$)-C$\underline{H}$(CH$_3$)$_2$), 1.63 (3H, d,

J=9 Hz, CH(C$\underline{H}_3$)), 3.2—4.0 (2H, m, N-CH$_2$–), 3.85 (2H, s, ring H), 3.95 (2H, s, ring H), and 7.20 (1H, s, NH).

Found: C, 60.45; H, 8.80%. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15%.

Photoadducts of 3,3-Dimethyl-1-butene (**5**) *with* **1**. *1,4-Bis(2-bromo-3,3-dimethylbutyl)-2,5-piperazinedione (5″**a**)*: Mp 226—227 °C (from benzene-acetone). IR, 1675, 1475, 1330, 1290, 1185, and 1110 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=1.11 (18H, s, C(CH$_3$)$_3$), 3.21 (2H, dd, J=11 and 15 Hz, N-CH$_2$–), 4.00 and 4.40 (center) (4H, AB quartet, J=16 Hz, ring H), 4.17 (2H, dd, J=2 and 15 Hz, N-CH$_2$–), and 4.26 (2H, dd, J=2 and 11 Hz, -CHBr-).

Found: C, 43.85; H, 6.46%. Calcd for $C_{16}H_{28}Br_2N_2O_2$: C, 43.65; H, 6.36%.

*5″**b***: Mp 242—243 °C (from benzene-acetone). IR, 1670, 1475, 1335, 1280, 1185, and 1120 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=1.12 (18H, s, C(CH$_3$)$_3$), 3.29 (2H, dd, J=11 and 15 Hz, N-CH$_2$–), 3.98 and 4.42 (center) (4H, AB quartet, J=16 Hz, ring H), 4.18 (2H, dd, J=2 and 15 Hz, N-CH$_2$–), and 4.29 (2H, dd, J=2 and 11 Hz, -CHBr-).

Found: C, 43.85; H, 6.62%. Calcd see above.

1-(2-Bromo-3,3-dimethylbutyl)-2,5-piperazinedione (5′): Mp 177—178 °C (from benzene and acetone). IR, 3230, 1670, 1465, 1320, 1280, and 1120 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=1.11 (9H, s, C(CH$_3$)$_3$), 3.25 (1H, dd, J=11 and 15 Hz, N-CH$_2$–), 3.99 and 4.42 (center) (2H, AB quartet, J=17 Hz, ring H), 4.03 (2H, s, ring H), 4.23 (1H, dd, J=3 and 15 Hz, N-CH$_2$–), 4.31 (1H, dd, J=3 and 11 Hz, -CHBr-), and 7.00 (1H, s, NH).

Found: C, 43.84; H, 6.62%. Calcd for $C_{10}H_{17}BrN_2O_2$: C, 43.33; H, 6.18%.

*1,4-Bis(3,3-dimethylbutyl)-2,5-piperazinedione (5″(**H**))*: Mp 190—191.5 °C (from benzene-hexane). IR, 1675, 1480, 1317, and 1285 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=0.98 (18H, s, C(CH$_3$)$_3$), 1.43 (4H, m, N-CH$_2$-C$\underline{H}_2$–), 3.36 (4H, m, N-CH$_2$–), and 3.86 (4H, s, ring H).

Found: C, 67.82; H, 10.68%. Calcd for $C_{16}H_{30}N_2O_2$: C, 68.04; H, 10.71%.

*1-(3,3-Dimethylbutyl)-2,5-piperazinedione (5′(**H**))*: Mp 223.5—224.5 ° (from benzene-hexane). IR, 3240, 1670, 1475, 1320, 1285, and 1120 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ=0.95 (9H, s, C(CH$_3$)$_3$), 1.42 (2H, m, N-CH$_2$-C$\underline{H}_2$–), 3.35 (2H, m, N-CH$_2$–), 3.88 (2H, s, ring H), 3.92 (2H, s, ring H), and 6.90 (1H, s, NH).

Found: C, 60.67; H, 8.94%. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15%.

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