Synthetic Photochemistry. LII.1) Substituent Effects of a Bromine Atom on the High-Pressure Cycloaddition between 1-Acetyl-7-bromocyclohepta[*b*]pyrrol-2(1*H*)-one and 2,3-Bis(methoxycarbonyl)-7-oxanorbornadiene and the Photorearrangement of 2-Acetyl-9-bromo-2-azatricyclo-[6.2.2.$0^{1,5}$]dodeca-4,6,9,11-tetraen-3-one

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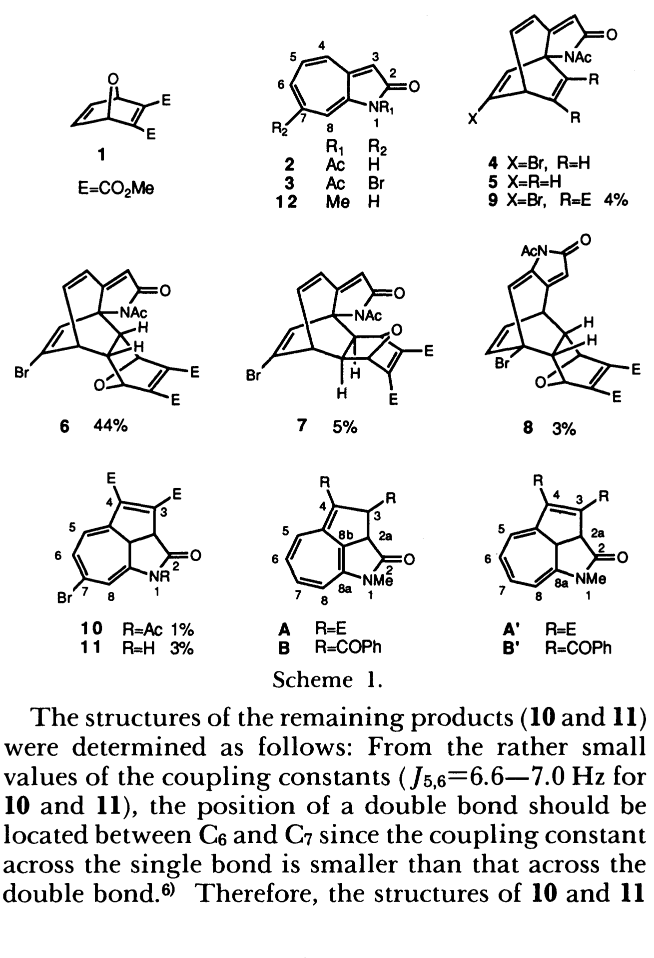
Synopsis. A high-pressure cycloaddition reaction of 1-acetyl-7-bromocyclohepta[*b*]pyrrol-2(1*H*)-one and 2,3-bis(methoxycarbonyl)-7-oxanorbornadiene and a further thermolysis of [4+2] cycloadducts gave 2-acetyl-9-bromo-2-azatricyclo[6.2.2.$0^{1,5}$]dodeca-4,6,9,11-tetraen-3-one, which was photorearranged to 9-methylenebarbaralane and 5-methylenetricyclo[4.3.0.$0^{2,9}$]nonadiene derivatives. The product distribution of the photolysis was altered by a bromine atom.

From a comparative point of view of the results of 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene (**1**) with 2*H*-cyclohepta[*b*]furan-2-ones, we investigated2) the reaction of **1** with 1-acetylcyclohepta[*b*]pyrrol-2(1*H*)-one (**2**) in order to observe both [4+2] and [8+2] cycloadducts, the latter of which are of interest in regard to a possible entry to azulene derivatives.3)

Since the introduction of an electronegative halogen substituent into a seven-membered ring may alter the reaction course, it should be worthwhile carrying out the reaction with an easily available bromo derivative of **2**. Herein, we describe the result for **1** and 1-acetyl-7-bromocyclohepta[*b*]pyrrol-2(1*H*)-one (**3**),4) disclosing that the heptafulvene structures, formerly proposed by Abe and Takehiro for [8+2] cycloadducts,5) were shown to be revised. Furthermore, the photorearrangement of 2-acetyl-9-bromo-2-azatricyclo[6.2.2.$0^{1,5}$]dodeca-4,6,9,11-tetraen-3-one (**4**), the cycloreversed product, gave a different product distribution from that of 2-acetyl-2-azatricyclo[6.2.2.$0^{1,5}$]dodeca-4,6,9,11-tetraen-3-one (**5**).2)

When a chlorobenzene solution of **1** and **3** was heated at 120 °C under 3000 bar, six products (**6**—**11**) were isolated. A major product (**6**) was an endo [4+2] cycloadduct from NMR spectral data, whereas product **7** was an exo [4+2] isomer. Product **8** was another endo [4+2] adduct, whose NMR spectrum closely resembled that of the corresponding adduct from **1** and **2**.2) Product **9** was formally an adduct between **3** and dimethyl butynedioate.



Scheme 1.

The structures of the remaining products (**10** and **11**) were determined as follows: From the rather small values of the coupling constants ($J_{5,6}$=6.6—7.0 Hz for **10** and **11**), the position of a double bond should be located between C_6 and C_7 since the coupling constant across the single bond is smaller than that across the double bond.6) Therefore, the structures of **10** and **11**

Table 1. NMR Data of **10**, **11** and Related Compounds **A′** and **B′**

	10	**11**	**A′**a)	**B′**a)
H_8	7.40 (s)	5.93 (s)	5.66 (d, 6.1)	5.73 (d, 6.1)
H_7	Br	Br	6.65—6.75	6.72 (dd, 9.8, 6.1)
H_6	6.33 (d, 6.6)	6.30 (d, 7.0)	6.4—6.5	6.35—6.45 (m)
H_5	6.99 (d, 6.6)	6.85 (d, 7.0)	6.4—6.5	6.35—6.45 (m)
H_{8b}	3.34 (d, 9.5)	3.35 (d, 8.8)	3.10 (d, 9.2)	3.32 (d, 9.2)
H_{2a}	4.41 (d, 9.5)	4.32 (d, 8.8)	4.32 (d, 9.2)	4.92 (d, 9.2)
MeO	3.88, 3.89	3.86, 3.88	3.86, 3.88	

a) See Ref. 4.

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Table 2. Electronic Spectral Data of **10**, **11**, **A′**, and **B′**[a]

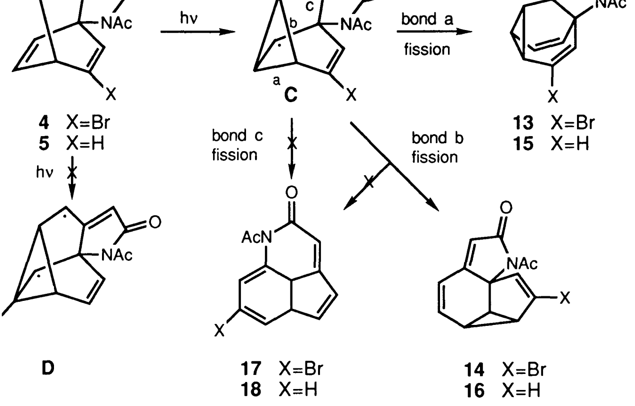
10	**11**	**A′**	**B′**
225.8 (11700)	234.0 (10100)	228.0 (21200)	227.6 (30600)
266.0 (11500)	274.2 (9400)	270.4 (19000)	258.0 (28400)
323.8 (5300)	400.4 (900)	314.0 (4100 sh)	322.8 (8200 sh)
361.8 (4200)	450.0 (500)	410.8 (3000)	422.0 (3300)
425.0 (240)			

a) Measured in methanol.

were determined as shown in Scheme 1. According to a recent paper regarding the reactions of 1-methylcyclohepta[*b*]pyrrol-2(1*H*)-one (**12**) and acetylenes,[5] heptafulvene structures **A** and **B** have been proposed on the basis of an NMR analysis. However, since their ^{1}H NMR and UV data were very similar to **10** and **11**, except for the appearance of an H$_7$ proton and up-field shifted neighboring proton signals (Tables 1 and 2[7]), they should be revised to **A′** and **B′**. In the new structures the values of the coupling constants ($J_{6,7}$=9.8 Hz and $J_{7,8}$=6.1 Hz for **B**) are more consistent and the chemical shifts of H$_8$ around 5.7 are reasonably explained in terms of the electron donation of the nitrogen atom. Furthermore, a small difference in the chemical shift between two methoxy groups and very large difference (over 1 ppm) in the chemical shift of two methine protons are also compatible with the revised structures.

In the reactions of **3** and **1**, the formations of [4+2] adducts were predominated over [8+2] adducts ([4+2]/[8+2]=56/4), while the ratio of [4+2] and [8+2] adducts was 14/16 from **2** and **1**.[2] Thus, the chemical reactivity of **3** toward **1** was different from that of **2**.

The thermal cycloreversion of **6** afforded **4**, the structure of which was elucidated by comparison with spectral data of **5**.[2] The irradiation of **4** with a 400-W high-pressure mercury lamp gave two products (**13** and **14**). The structures of **13** and **14** were determined to be substituted 9-methylenebarbaralane and 5-methylenetricyclo[4.3.0.0^{2,9}]nonadiene derivative by a comparison with the spectral data of **15** and **16**.[2] Among the photoproducts from **4**, a methylenedihydroindene derivative (**17**) was not detected, despite an intensive effort. This was in contrast to the fact that **5** gave a methylenedihydroindene derivative (**18**).



Scheme 2.

The mechanism of the photorearrangement of **4** was considered to be similar to that of **5**.[2] There are two bridging sites between the extended enone and an etheno bridge in **4**. The structure of **14** indicated that the bridging occurred at the etheno bridge carrying no bromine atom to give the intermediate (**C**). Certainly, the bromine atom prevented sterically the formation of the bridged intermediate (**D**).

On the other hand, an absence of methylenedihydroindene derivative, **17**, in the photorearrangement of **4** suggests that **13** and **14** were products via a triplet state: Namely, it has already been clarified, in the photorearrangement of 2-oxatricyclo[6.2.2.0^{1,5}]dodeca-4,6,9,11-tetraen-3-ones,[8] that methylenedihydroindenes were formed via a singlet excited state, and it was conceivable that the intersystem crossing of the singlet state to the triplet one would be facilitated for the brominated **4**, diminishing the formation of methylenedihydroindene **17**.[9]

Experimental

Cycloaddition Reaction of 1 and 3 under 3000 bar. A chlorobenzene solution (2.5 cm^3) of **1** (320 mg) and **3** (150 mg) was heated at 120 °C under 3000 bar for 20 h. The solvent was evaporated under reduced pressure and the residue was purified via silica-gel column chromatography, which followed by HPLC, to give **6** (98.5 mg, 44%), **7** (12 mg, 5%), **8** (7 mg, 3%), **9** (7 mg, 4%), **10** (2.4 mg, 1%), **11** (5.4 mg, 3%), and recovered **3** (26.3 mg).

6: Colorless crystals, mp 191—193 °C; ^{1}H NMR[10] δ=2.25 (1H, dd, J=8.8, 0.7 Hz), 2.54 (1H, dd, J=8.8, 1.1 Hz), 2.66 (3H, s), 3.63 (1H, dm, J=8.4 Hz), 3.78 (3H, s), 3.81 (3H, s), 5.04 (1H, d, J=1.1 Hz), 5.70 (1H, s), 5.78 (1H, s), 6.31 (1H, d, J=10.3 Hz), 6.49 (1H, dd, J=1.1, 0.7 Hz), and 6.77 (1H, dd, J=10.3, 8.4 Hz); ^{13}C NMR δ=26.6, 47.0, 49.1, 50.5, 52.5 (2C), 72.4, 83.6, 85.4, 118.4, 120.4, 123.3, 127.2, 141.8, 144.6, 146.4, 158.3, 162.6, 162.7, 170.2, and 171.4; IR 1720, 1635, and 1285 cm^{-1}; UV (MeOH) 245.8 (ε 8600) and 285.6 nm (6300). Found: C, 53.01; H, 3.84; N, 2.75%. Calcd for $C_{21}H_{18}NO_7Br$: C, 52.96; H, 3.81; N, 2.94%.

7: Colorless crystals, mp 223 °C; ^{1}H NMR δ=2.64 (3H, s), 2.80 (1H, dd, J=8.8, 5.8 Hz), 3.68 (1H, d, J=8.8 Hz), 3.76 (3H, s), 3.8 (1H, m), 3.82 (3H, s), 4.57 (1H, d, J=1.1 Hz), 4.86 (1H, d, J=1.1 Hz), 5.88 (1H, s), 6.37 (1H, d, J=1.8 Hz), 6.46 (1H, dd, J=10.3, 8.8 Hz), and 6.55 (1H, dd, J=10.3, 1.8 Hz); ^{13}C NMR δ=25.8, 43.0, 47.2, 47.6, 52.4, 52.6, 72.0, 79.8, 83.3, 119.6, 124.6, 127.5, 131.5, 135.9, 145.5, 145.7, 157.0, 161.7, 162.4, 169.8, and 170.1; IR 1720, 1630, and 1280 cm^{-1}; UV (MeOH) 244.2 (ε 9600) and 283.6 nm (7500). Found: C, 53.11; H, 3.84; N, 2.87%. Calcd for $C_{21}H_{18}NO_7Br$: C, 52.96; H, 3.81; N, 2.94%.

8: Colorless crystals, mp 183—184 °C; ^{1}H NMR δ=2.47 (1H, d, J=7.7 Hz), 2.55 (3H, s), 3.11 (1H, d, J=7.7 Hz), 3.81 (3H, s), 3.83 (1H, d, J=8.1 Hz), 3.85 (3H, s), 5.12 (1H, d, *J*=1.5 Hz), 5.52 (1H, d, *J*=1.5 Hz), 5.91 (1H, d, *J*=1.8 Hz), 5.96 (1H, ddm, *J*=9.2, 8.1 Hz), 6.63 (1H, d, *J*=9.2 Hz), and 8.00 (1H, d, *J*=1.8 Hz); ^{13}C NMR δ=26.6, 39.8, 46.0, 52.6 (2C), 57.3, 61.1, 86.5, 86.7, 116.4, 126.4, 132.0, 135.5, 142.0, 144.8, 146.1, 152.1, 162.3, 162.5, 168.0, and 170.8; IR 1715, 1600, and 1305 cm^{-1}; UV (MeOH) 240.2 (ε 9100) and 274.0 nm (8200).

Found: C, 53.07; H, 3.84; N, 2.88%. Calcd for $C_{21}H_{18}NO_7Br$: C, 52.96; H, 3.81; N, 2.94%.

9: Colorless crystals, mp 189 °C; ^{1}H NMR δ=2.56 (3H, s), 3.72 (3H, s), 3.79 (3H, s), 4.43 (1H, dd, *J*=8.1, 2.2 Hz), 5.92 (1H, s), 6.19 (1H, d, *J*=10.3 Hz), 6.40 (1H, d, *J*=2.2 Hz), and 6.66 (1H, dd, *J*=10.3, 8.1 Hz); ^{13}C NMR δ=24.8, 48.8, 52.7, 53.0, 70.7, 121.0, 122.1 (2C), 122.6, 130.5, 135.3, 136.6, 148.5, 163.5, 164.4, 168.6, and 169.6; IR 1725, 1435, 1370, and 1300 cm^{-1}; UV (MeOH) 234.4 (ε 11900) and 285.7 nm (sh 6100).

Found: *m/z* 407.0008 (M$^+$ for ^{79}Br) and 409.0049 (M$^+$ for ^{81}Br). Calcd for $C_{17}H_{14}NO_6Br$: 407.0005 (M for ^{79}Br) and 408.9984 (M for ^{81}Br).

10: A colorless oil; IR 1760, 1725, 1610, 1590, and 1220 cm^{-1}.

Found: *m/z* 406.9999 (M$^+$ for ^{79}Br) and 408.9955 (M$^+$ for ^{81}Br). Calcd for $C_{17}H_{14}NO_6Br$: 407.0002 (M for ^{79}Br) and 408.9992 (M for ^{81}Br).

11: A colorless oil; IR 1720, 1430, and 1280 cm^{-1}.

Found: *m/z* 364.9904 (M$^+$ for ^{79}Br) and 366.9807 (M$^+$ for ^{81}Br). Calcd for $C_{15}H_{12}NO_5Br$: 364.9900 (M for ^{79}Br) and 366.9877 (M for ^{81}Br).

DDQ-Oxidation of 10. A C_6D_6 solution (0.5 cm^3) of **10** (1.5 mg) and DDQ (3 mg) was heated at 80 °C for 4 h in a NMR tube. The reaction was monitored by the ^{1}H NMR spectra. No change was observed.

Thermal Cycloreversion of 6. A chlorobenzene solution (1 cm^3) of **6** (60 mg) was heated for 24 h at 130 °C. The solvent was evaporated and the residue was chromatographed on a silica-gel column and HPLC to give **4** (24 mg, 65%) and 3,4-bis(methoxycarbonyl)furan (16 mg, 69%).

4: A colorless oil; ^{1}H NMR δ=2.61 (3H, s), 3.94 (1H, tm, *J*=8.0 Hz), 5.79 (1H, s), 6.05 (1H, d, *J*=10.3 Hz), 6.25 (1H, dt, *J*=7.0, 1.1 Hz), 6.37 (1H, d, *J*=1.1 Hz), 6.52 (1H, dd, *J*=8.0, 7.0 Hz), and 6.65 (1H, dd, *J*=10.3, 8.0 Hz); ^{13}C NMR δ=25.1, 48.9, 70.8, 119.1, 120.8, 123.3, 131.1, 131.5, 137.7, 151.2, 169.4, and 169.5; IR 1720, 1700, 1685, and 1290 cm^{-1}; UV (MeOH) 264.2 nm (ε 8200).

Found: *m/z* 290.9925 (M$^+$ for ^{79}Br) and 292.9824 (M$^+$ for ^{81}Br). Calcd for $C_{13}H_{10}NO_2Br$: 290.9896 (M for ^{79}Br) and 292.9875 (M for ^{81}Br).

Photorearrangement of 4. A $CDCl_3$ solution (0.5 cm^3) of **4** (65 mg) was irradiated with a 400-W high-pressure mercury lamp for 2.5 h. After the evaporation of the solvent, the residue was chromatographed on a silica-gel column and HPLC to give **13** (10 mg, 24%), **14** (5.6 mg, 14%), and recovered **4** (21 mg).

13: A colorless oil, ^{1}H NMR δ=2.57 (3H, s), 2.86 (1H, m), 3.01 (1H, td, *J*=7.7, 2.2 Hz), 3.13 (1H, dd, *J*=7.7, 7.0 Hz), 5.76 (1H, s), 5.84 (1H, dd, *J*=9.2, 6.2 Hz), 6.38 (1H, dd, *J*=9.2, 0.7 Hz), and 6.56 (1H, d, *J*=2.2 Hz); ^{13}C NMR δ=21.8, 25.2, 29.9, 37.0, 67.5, 111.3, 114.2, 119.7, 127.7, 129.0, 159.5, 169.1, and 169.7; IR 1730, 1695, 1660, 1380, and 1305 cm^{-1}; UV (MeOH) 274.8 (ε 16900) and 273.6 nm (2400).

Found: *m/z* 290.9929 (M$^+$ for ^{79}Br) and 292.9824 (M$^+$ for ^{81}Br). Calcd for $C_{13}H_{10}NO_2Br$: 290.9896 (M for ^{79}Br) and 292.9875 (M for ^{81}Br).

14: Colorless crystals, mp 153 °C; ^{1}H NMR δ=2.16 (1H, td, *J*=7.3, 4.4 Hz), 2.55 (3H, s), 2.81 (1H, ddm, *J*=7.3, 6.6 Hz), 3.02 (1H, dd, *J*=7.3, 6.6 Hz), 5.21 (1H, d, *J*=0.7 Hz), 5.71 (1H, s), 6.24 (1H, dd, *J*=9.9, 4.4 Hz), and 6.65 (1H, d, *J*=9.9 Hz); ^{13}C NMR δ=25.4, 26.2, 37.3, 45.8, 73.4, 115.4, 122.6, 123.3, 130.9, 132.7, 159.3, 169.5, and 169.6; IR 1725, 1635, 1600, 1375, and 1305 cm^{-1}; UV (MeOH) 231.6 (ε 9975) and 298.0 nm (4800).

Found: *m/z* 290.9917 (M$^+$ for ^{79}Br) and 292.9824 (M$^+$ for ^{81}Br). Calcd for $C_{13}H_{10}NO_2Br$: 290.9896 (M for ^{79}Br) and 292.9875 (M for ^{81}Br).

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7) It was true that an introduction of a bromine atom at C_7 made the ^{1}H NMR analysis of these derivatives easier.

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9) A referee suggested that **17** should be formed rather via a bond b fission and the following bond c fission than via a bond c and the following bond b fissions. However, we have no experimental evidence to distinguish them.

10) NMR spectra were measured with JEOL FX 100 Model and GSX 270 H Model spectrometers in a $CDCl_3$ solution.