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Side-Chain Bromination of Diphenylmethanes, 1,2-Diphenylethanes, and 10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptenes with *N*-Bromosuccinimide under Irradiation of a Tungsten Lamp

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Synopsis. The photothermal bromination of diphenylmethane and methyl derivatives with *N*-bromosuccinimide afforded benzophenone and (polybromomethyl)benzophenones via the hydrolysis of dibromodiphenylmethanes. 1,2-Diphenylethane and *p*-*t*-butyl derivative gave dibromostilbenes, while the *o*-methyl derivative afforded bis(dibromomethyl)dibromodiphenylethane. 10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene gave 9-bromodibenzocycloheptenone, which was also obtained in the bromination of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one.

It was previously reported that the photothermal polybromination of methyl-, dimethyl-, and trimethylbenzenes with NBS (*N*-bromosuccinimide) gave (dibromomethyl)arenes and (tribromomethyl) derivatives, depending upon the solvent used and the substituent on the benzene ring.[1] The monobromination of diphenylmethane was carried out with NBS in carbon tetrachloride, as earlier reported.[2] Also, the thermal bromination of 1,2-diphenylethane with NBS was reported to give stilbene, together with stilbene dibromide as a by-product.[3]

Here, the photothermal polybromination of diphenylmethanes, 1,2-diphenylethanes, and their cyclic analogue, 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene is reported.

Results and Discussion

Diphenylmethanes **1a**—**e** gave the corresponding benzophenones **2b**—**e** in photothermal bromination with an appropriate amount of NBS (Table 1) in benzene under irradiation with a tungsten lamp. It was deduced that moisture-labile dibromodiphenylmethane might be hydrolyzed during the work-up, giving **2**. The addition of methanolic sodium methoxide to the bromination mixture of **1a** before the work-up afforded the expected dimethoxydiphenylmethane in 22% yield, together with **1a** and **3a**. The regiochemistry of by-product **3b** is unknown (Scheme 1).

Each two ortho-methyl groups of diphenylmethanes **4a**,**b** were dibrominated. These facts are in accord with the previous observation[1] that an ortho-substituent interrupts the tribromination of the neighboring methyl groups; benzophenones **5a**,**b** were obtained (Chart 1). Also, the ortho-methyl substituted benzophenone, **6a** and **6b**, gave the *o*-(dibromomethyl) derivatives **7a** and **7b**. Even when 3.3 equivalents of NBS were employed, **6a** produced **7a** (67% yield). The methyl group of the meta derivative **8** was tribrominated, as expected, giving **9**.

In the bromination of dimethyldiphenylmethane **10** and dimethylbenzophenone **14**, it was shown that the carbonyl function assists the polybromination of a methyl group in **14**, probably due to a stabilization of the radical intermediates[4,5] in each step. When being brominated with 8.4 equivalents of NBS, **10** gave a mixture of bis(polybromomethyl)benzophenone **11**, **12**, and **13**, in which 4,4′-bis(dibromomethyl)benzophenone (**12**) is the major product. On the other hand, the 4,4′-bis(tribromomethyl) derivative **15** was the major product in the bromination of **14**. The polybromination of **14** to **15** proceeds stepwise via **11**, **12**, and **13** (Table 1).

When 1,2-diphenylethanes **16a**,**b** were brominated, (*E*)-α,β-dibromostilbenes **17a**,**b** were produced. It was deduced that **17a**,**b** were formed via the bromination of 1,2-dibromo-1,2-diphenylethanes **18a**,**b** followed by dehydrobromination. Indeed, *meso*-**18a** gave **17a** (Scheme 2). On the other hand, the 1,2-bis(2-methylphenyl) derivative **16c** gave 1,2-dibromo-1,2-bis(2-dibromomethyl-4-*t*-butylphenyl)ethane (**18c**). It may be difficult, due to steric reasons, to brominate the 1,2-dibromoethano bridge of **18c**.

Finally, the bromination of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene **19**, which have both the diphenylmethane and diphenylethane moieties, gave 9-bromobenzocycloheptenone **20**[6] in poor yield. Compound **20** was obtained in the bromination of the corresponding ketone **21** in a much better yield (79%).

Experimental

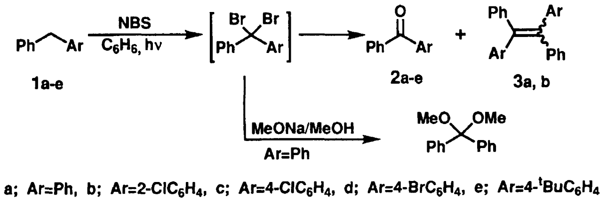
All of the melting points were measured on a Mitamurariken Melt Thermo, and were uncorrected. The IR spectra were measured on a Nippon-Bunko IR-700 as a KBr pellet unless otherwise stated. The NMR spectra were recorded at 270 MHz with a JEOL GSX-270 using TMS as an internal standard in $CDCl_3$, unless otherwise stated. The mass spectra were obtained on a JEOL JMS-O1SG-2 mass spectrometer at 75 ev using a direct inlet system.

Photobromination. General Procedure: The mixture of a substrate (10 mmol), the appropriate amount of NBS given in Table 1, and AIBN (10 mg) in benzene (100 cm^3) was irradiated with a tungsten lamp (Nikko Electron

Table 1. Photothermal Bromination

Substrate	NBS[a)]	Time[b)]	Product (%)	Substrate	NBS[a)]	Time[b)]	Product (%)
1a	2.2	10	**2a**(70), **3a**(14)	**10**	8.4	20	**11**(12), **12**(43)
1b	2.2	16	**2b**(85), **3b**(6)				**13**(20)
1c	2.2	14	**2c**(76)	**14**	6.4	18	**12**(12), **13**(17)
1d	2.2	14	**2d**(82)				**15**(51)
1e	2.2	10	**2e**(78)		9.4	18	**13**(17), **15**(60)
4a	8.4	20	**5a**(73)	**16a**	4.4	19	**17a**(57)
4b	8.4	18	**5b**(71)	**16b**	4.4	18	**17b**(73)
6a	2.2	16	**7a**(65)	**16c**	10.4	17	**18c**(74)
6b	6.4	20	**7b**(62)	**18a**[c)]	2.2	12	**17a**(53)
8	3.3	15	**9**(82)	**19**[d)]	6.4	22	**20**(28)
				21	4.4	16	**20**(79)

a) Molar ratio of NBS/substrate. b) Hour. c) Recovered in 15% yield. d) Recovered in 39% yield.



Scheme 1.

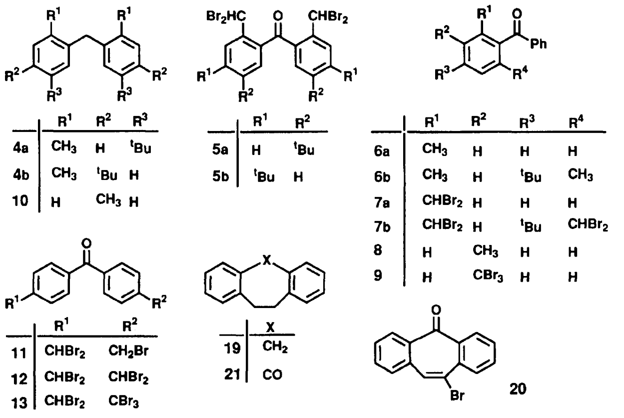
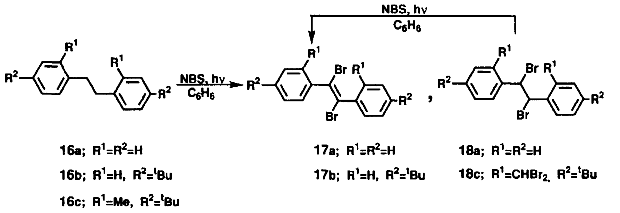


Chart 1.



Scheme 2.

Co., Ltd., RF-110 V/500 WH) without external cooling, while stirring for the time given in Table 1. Then, succinimide was filtered off and dilute aqueous sodium hydrogensulfite was added to the filtrate. The organic layer was separated and dried over $MgSO_4$. After removing the solvent, the residue was chromatographed on silica gel (Wako gel), giving the products. The compounds were eluted with hexane–benzene (2/1 volume ratio). The physical and spectral properties of new compounds are given below.

A Mixture of (*E*)- and (*Z*)-1,2-bis(*p*-chlorophenyl)-1,2-diphenylethene (3b): Colorless prisms (benzene); mp 178—190 °C; ^{1}H NMR δ=6.91—7.14 (m); ^{13}C NMR δ=126.81, 126.90, 127.11, 127.81, 127.94, 127.99, 128.12, 128.19, 131.05, 131.12, 131.21, 132.37, 132.54, 132.74, 132.85, 140.25, 141.92, and 142.93; MS *m*/*z* (rel intensity) 404 (M$^+$; 13), 402 (M$^+$; 64), and 400 (M$^+$; 100).

Found: C, 77.50; H, 4.64%. Calcd for $C_{26}H_{18}Cl_2$: C, 77.79; H, 4.52%.

2,2′-Bis(dibromomethyl)-5,5′-di-*t*-butylbenzophenone (5a): Colorless needles (hexane); mp 190—193 °C; IR 1653 cm^{-1}; ^{1}H NMR δ=1.24 (18H, s), 7.18 (2H, d, *J*=2.0 Hz), 7.46 (2H, s), 7.69 (2H, dd, *J*=8.5 and 2.0 Hz), and 8.15 (2H, d, *J*=8.5 Hz); ^{13}C NMR δ=30.93, 34.78, 37.83, 127.60, 130.04, 131.35, 133.38, 139.58, 152.36, and 198.67.

Found: C, 43.25; H, 4.14%. Calcd for $C_{23}H_{26}OBr_4$: C, 43.29; H, 4.11%.

2,2′-Bis(dibromomethyl)-4,4′-di-*t*-butylbenzophenone (5b): Colorless needles (hexane); mp 129—132 °C; IR 1652 cm^{-1}; ^{1}H NMR δ=1.40 (18H, s), 7.17 (2H, d, *J*=8.3 Hz), 7.33 (2H, dd, *J*=1.6 and 8.3 Hz), 7.51 (2H, s), and 8.24 (2H, d, *J*=1.6 Hz); ^{13}C NMR δ=30.94, 35.40, 38.42, 125.93, 128.77, 130.62, 131.18, 142.32, 156.71, and 197.82.

Found: C, 43.22; H, 4.11%. Calcd for $C_{23}H_{26}OBr_4$: C, 43.29; H, 4.11%.

2-(Dibromomethyl)benzophenone (7a): Colorless oil; IR (NaCl) 1660 cm^{-1}; ^{1}H NMR δ=7.14 (1H, s), 7.27—7.30 (1H, m), 7.35—7.40 (1H, m), 7.45—7.49 (2H, m), 7.60—7.65 (2H, m), 7.81 (2H, dd, *J*=6.8 and 1.0 Hz), and 8.18 (1H, dd, *J*=7.0 and 1.0 Hz); ^{13}C NMR δ= 37.59, 126.61, 128.75, 128.91, 130.46, 131.10, 131.71, 133.74, 134.09, 137.07, 141.48, and 196.73.

Found: C, 47.20; H, 2.88%. Calcd for $C_{14}H_{10}OBr_2$: C, 47.49; H, 2.85%.

2,6-Bis(dibromomethyl)-4-*t*-butylbenzophenone (7b): Yellow prisms (benzene); mp 156—158 °C; IR 1665 cm^{-1}; ^{1}H NMR δ=1.46 (9H, s), 6.37 (2H, s), 7.50 (2H, dd, *J*=7.6 and 7.6 Hz), 7.66 (1H, d, *J*=7.4 Hz), 7.83 (2H, d, *J*=7.4 Hz), and 8.09 (2H, s); ^{13}C NMR δ=32.27, 36.73, 37.74, 129.36, 130.24, 130.46, 131.48, 136.55, 137.25, 139.37, 156.14, and 197.18.

Found: C, 39.15; H, 3.26%. Calcd for $C_{19}H_{18}OBr_4$: C, 39.21; H, 3.26%.

3-(Tribromomethyl)benzophenone (9): Colorless needles (hexane); mp 95—96 °C; IR 1652 cm^{-1}; ^{1}H NMR δ=7.48—7.66 (4H, m), 7.75—7.85 (3H, m), 8.23 (1H, ddd, *J*=8.0, 1.0 and 1.0 Hz), and 8.44 (1H, dd, *J*=2.0 and 2.0 Hz);

^{13}C NMR δ=34.79, 127.90, 128.07, 128.26, 128.50, 130.10, 131.46, 132.92, 136.87, 137.41, 147.17, and 195.25.

Found: C, 39.06; H, 2.13%. Calcd for $C_{14}H_9OBr_3$: C, 38.84; H, 2.10%.

4-(Bromomethyl)-4′-(dibromomethyl)benzophenone (11): Colorless needles (hexane); mp 108—110 °C; IR 1650 cm^{-1}; ^{1}H NMR δ=4.53 (2H, s), 6.69 (1H, s), 7.51 (2H, d, J=8.0 Hz), 7.68 (2H, d, J=8.2 Hz), and 7.76—7.81 (4H, m); ^{13}C NMR δ=32.51, 39.69, 126.59, 129.05, 130.29, 130.51, 136.85, 138.38, 142.50, 145.58, and 197.71; MS m/z (rel intensity) 448 (M^+; 3), 446 (M^+; 3), 369 (50), 367 (100), and 365 (51).

Found: C, 40.17; H, 2.57%. Calcd for $C_{15}H_{11}OBr_3$: C, 40.31; H, 2.48%.

4,4′-Bis(dibromomethyl)benzophenone (12): Colorless needles (hexane); mp 120—122 °C; IR 1652 cm^{-1}; ^{1}H NMR δ=6.69 (1H, s), 7.70 (2H, d, J=8.2 Hz), and 7.80 (2H, d, J=8.2 Hz); ^{13}C NMR δ=39.57, 126.70, 130.35, 138.09, 145.82, and 194.32; MS m/z (rel intensity) 528 (M^+; 1), 526 (M^+; 2), 524 (M^+; 1), 449 (33), 447 (99), 445 (100), and 443 (34).

Found: C, 34.36; H, 2.00%. Calcd for $C_{15}H_{10}OBr_4$: C, 34.26; H, 1.92%.

4-(Dibromomethyl)-4′-(tribromomethyl)benzophenone (13): Colorless needles (hexane); mp 190—192 °C; IR 1651 cm^{-1}; ^{1}H NMR δ=6.70 (1H, s), 7.71 (2H, d, J=8.6 Hz), 7.81—7.85 (4H, m), and 8.16 (2H, d, J=8.6 Hz); ^{13}C NMR δ=34.52, 39.53, 126.70, 126.75, 129.65, 130.38, 137.93, 138.20, 145.96, 150.28 and 194.05.

Found: C, 30.09; H, 1.58%. Calcd for $C_{15}H_9OBr_5$: C, 29.79; H, 1.50%.

4,4′-Bis(dibromomethyl)benzophenone (15): Colorless needles (benzene); mp 268—270 °C; IR 1649 cm^{-1}; ^{1}H NMR δ=7.85 (2H, d, J=8.9 Hz) and 8.15 (2H, d, J=8.9 Hz); ^{13}C NMR δ=34.43, 126.76, 129.69, 138.04, 150.40, and 193.80; MS m/z (rel intensity) 529 (M^+; 18), 527 (M^+; 68), 525 (M^+; 100), 523 (M^+; 72), and 521 (M^+; 18).

Found: C, 26.37; H, 1.32%. Calcd for $C_{15}H_8OBr_6$: C, 26.35; H, 1.18%.

(*E*)-α,β-Dibromo-4,4′-di-*t*-butylstilbene (17b): Colorless plates (benzene); mp 212—215 °C; ^{1}H NMR δ= 1.35 (18H, s), 7.43 (4H, d, J=8.6 Hz), and 7.46 (4H, d, J=8.6 Hz); ^{13}C NMR δ=31.11, 34.79, 117.86, 125.23, 128.84, 137.91, and 151.93; MS m/z (rel intensity) 452 (M^+; 38), 450 (M^+; 75), 448 (M^+; 38) and 290 (100).

Found: C, 58.71; H, 5.79%. Calcd for $C_{22}H_{26}Br_2$: C, 58.68; H, 5.82%.

1,2-Dibromo-1,2-bis(2-dibromomethyl-4-*t*-butylphenyl)ethane (18c): Colorless needles (hexane); mp 288—290 °C; ^{1}H NMR δ=1.34 (18H, s), 6.20 (2H, s), 6.91 (2H, s), 7.41 (2H, d, J=8.3 Hz), and 7.67 (4H, d, J=8.3 Hz); ^{13}C NMR δ=31.07, 34.93, 37.54, 49.25, 127.48, 127.79, 132.13, 134.61, and 152.99.

Found: C, 36.55; H, 3.57%. Calcd for $C_{24}H_{34}Br_6$: C, 36.21; H, 3.55%.

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