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Photothermal Side-Chain Bromination of Methyl-, Dimethyl-, and Trimethylbenzenes with *N*-Bromosuccinimide

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Tri- and dibromination of methyl-, dimethyl-, and trimethylbenzenes with *N*-bromosuccinimide were accomplished by photothermal reaction with a tungsten lamp in carbon tetrachloride or benzene. (Dibromomethyl)arenes and (tribromomethyl) derivatives were produced depending upon a solvent used and a substituent on the benzene ring. In the bromination of methylbenzenes without a substituent on the ortho-position, (tribromomethyl)benzenes were formed. On the other hand, ortho-substituted methylbenzenes gave (dibromomethyl)benzenes. α,β-Dibromo-1,2-diarylstilbenes were formed via the debrominative carbon–carbon coupling reaction of (tribromomethyl) benzenes upon irradiation with a tungsten lamp.

Mono- and dibromination of a methyl group on arenes are usually accomplished, photochemically and thermochemically, by using *N*-bromosuccinimide (NBS).[1—3] On the other hand, tribrominations have been done so far only under harsh conditions by using bromine or carbon tetrabromide, and only a few papers[4—6] deal with the preparation of (tribromomethyl)arenes using NBS; earlier some of us reported in a preliminary communication that (tribromomethyl)arenes are accessible via a photothermal bromination of methylarenes with NBS in carbon tetrachloride using a tungsten lamp as the light source.[6] This paper describes the results of a further investigation on the photothermal polybromination of methyl- **1**, dimethyl- **2**—**4**, and trimethylbenzenes **5**—**6** with NBS and includes full details of our earlier communication.

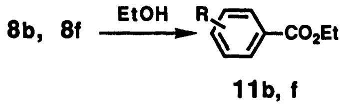
Results and Discussion

Bromination of Methylbenzenes 1. The results of the bromination of methylbenzenes **1** are summarized (Scheme 1 and Table 1).

A mixture of (dibromomethyl) benzene (**7a**), (tribromomethyl) derivative **8a**, (*Z*)-α,β-dibromostilbene (**9a**),[7] and its (*E*)-isomer **10a**[7,8] were formed in an early stage of the reaction of toluene (**1a**) with 3.1 molar amounts of NBS in carbon tetrachloride. The dibromide **7a** disappeared after 2.5 h and tribromide **8a** was obtained as the major product (64% yield). A prolonged irradiation (8 h) gave a rise in the yield of **9a** and **10a** with a decrease of the yield of **8a**. The reaction in benzene is slower than the reaction in carbon tetrachloride and after 8 h, a mixture of **7a**, **8a**, **9a**, and **10a** was given.

The formation pathway of **9a** and **10a** is given in Scheme 2; the cleavage of a C–Br bond of the tribromomethyl group in **8a** gives a dibromomethyl radical **A**, which attacks **8**, giving the coupling products **9** and **10** via a subsequent debromination. The formation of **A** is supported by the following facts: The photothermal reaction of **8a** in chloroform for 4 h gave a mixture of **7a**, **8a**, **9a**, and **10a** in the ratio of 23 : 59 : 9 : 9 and the reaction **8a** for 3 h in benzene in the presence of 3.1 equimolar amounts of succinimide as a hydrogen donor gave a mixture of **7a**, **8a**, **9a**, and **10a** in the ratio of 6 : 87 : 3.5 : 3.5. These ratios were measured by ^{1}H NMR.

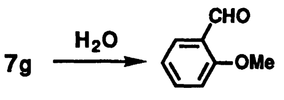
Meta- and para-substituted toluenes **1b**—**1f** similarly gave dibromides **7d** and **7f**, tribromides **8b**—**f**, and stilbenes **9c**—**f** and **10c**—**f**, depending upon the solvent used as shown in Table 1. The yields of moisture-sensitive tribromides **8b** and **8f** were measured as ethyl benzoates **11b**[9] and **11f**[10] (Eq. 1).



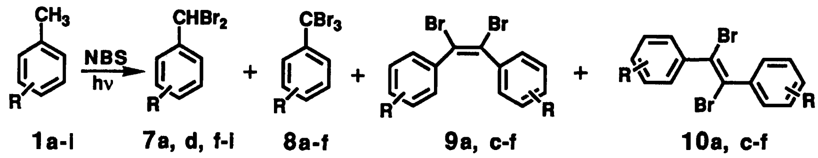
11b, f
b; R=p-MeO
f; R=m-NO$_2$ (1)

The configurations of stilbenes **9** and **10** were assigned on the basis of their ^{1}H NMR spectra. Aromatic protons[11] of **9a** appeared at about 0.3—0.4 ppm higher magnetic field than those[11] of **10a**. This is due to effective shielding of aromatic protons by the other benzene ring in the *Z*-configuration, as previously reported in (*E*)- and (*Z*)-α,β-dichlorostilbene derivatives.[12] Thus, **9**, showing aromatic protons in higher magnetic field, was assigned to be (*Z*)-α,β-dibromostilbene and **10** to be the (*E*)-isomer.

A substituent on the ortho position of **1g**—**i** hinders the tribromination, probably due to steric reasons. Dibromides **7g**—**i** were obtained as the sole product in 68—80% yield, even when a 3-fold amount of NBS was used. The yield of labile **7g** was given as 2-methoxybenzaldehyde (Eq. 2). A similar reaction of **1h** using a mercury lamp has been reported previously,[13] giving **7h** in 95% yield.



(2)



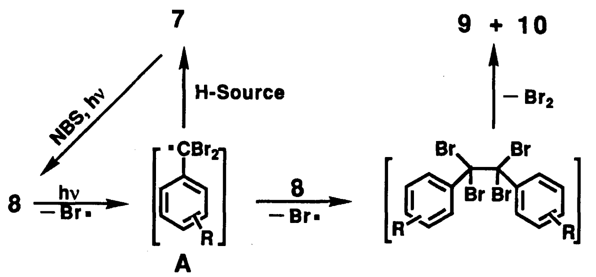
a; R=H, b; R=p-MeO, c; R=p-Br, d; R=p-NO_2, e; R=m-Br,
f; R=m-NO_2, g; R=o-MeO, h; R=o-Br, i; R=o-NO_2

Scheme 1.

Table 1. Bromination of Methylbenzenes **1**[a)]

1	R	Solvent	NBS/**1**[b)]	Time[c)]	Products, yield[d,e)] (%)
a	H	CCl_4	3.1	0.5	**7a**[f)] (39), **8a**[g)] (53), **9a**[h)]+**10a**[h)] (8)
				1.5	**7a** (5), **8a** (82), **9a**+**10a** (13)
				2.5	**8a** 64, **9a** 4, **10a** 3
				4	**8a** (78), **9a**+**10a** (22)
				8	**8a** (60), **9a**+**10a** (40)
		Benz[i)]	3.1	2.5	**7a** (29), **8a** (62), **9a**+**10a** (9)
				4	**7a** (23), **8a** (65), **9a**+**10a** (12)
				8	**7a** 11 (20), **8a** 37 (60), **9a**+**10a** 10 (20)
b	*p*-MeO	CCl_4	3.1	0.5	**8b**[j)] 92
c	*p*-Br	CCl_4	3.3	2.5	**8c**[k)] 56, **9c** 5, **10c** 18
		Benz	3.1	8	**8c** 57, **9c**+**10c** 9
d	*p*-NO_2	Benz	3.1	8	**7d**[l)] 42, **8d**[m)] 14, **9d**+**10d** 10
e	*m*-Br	Benz	3.1	8	**8e** 53 **9e**+**10e** 11
f	*m*-NO_2	CCl_4	3.1	4	**8f**[j)] 46, **9f** 22, **10f** 25
		CCl_4	3.1	34	**8f** 7, **10f** 73
		Benz	3.1	8	**7f**[o)] 56, **8f** 6
g	*o*-MeO	CCl_4	2.1	1.5	**7g** 68
h	*o*-Br	Benz	3.1	8	**7h**[o)] 80
		CCl_4	2.1	1.5	**7h** 75
i	*o*-NO_2	Benz	3.1	8	**7i**[p)] 74

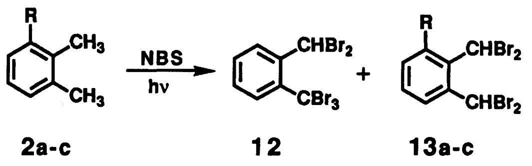
a) Ten milligrams of AIBN was used for every 0.01 mol of **1**. b) Molar ratio. c) Hour. d) Isolated yields are given unless otherwise started. e) Yields in parenthesis are relative yields measured by VPC and ^{1}H NMR. f) J. Hine and D. E. Lee, *J. Am. Chem. Soc.*, **73**, 22 (1951). g) W. H. Hunter and D. E. Edgar, *J. Am. Chem. Soc.*, **54**, 2025 (1932). h) Refs. 7 and 8. i) Benz means benzene. j) Measured as benzoated as stated in the text. k) M. Markarian, *J. Am. Chem. Soc.*, **74**, 1858 (1952). l) E. L. Eliel and K. W. Nelson, *J. Chem. Soc.*, **1955**, 1628. m) R. G. Jones, *J. Am. Chem. Soc.*, **69**, 2346 (1947). n) F. Kröhnke, H. Schmeiss, and W. Gottstein, *Chem. Ber.*, **84**, 131 (1951). o) Ref. 10. p) F. Marti, T. Somlo, and J. Gosteli, Ger. Offen., 2749800 (1978); *Chem. Abstr.*, **89**, 42739r (1978).



Scheme 2.

Bromination of Dimethylbenzenes 2—4. The results of the bromination of dimethylbenzenes **2**—**4** are shown in Schemes 3, 5, 6, and 7 and Table 2.

The bromination of *o*-xylene (**2a**) in carbon tetrachloride afforded exclusively the pentabromide **12**, while the reaction in anhydrous benzene gave a mixture of **12** and



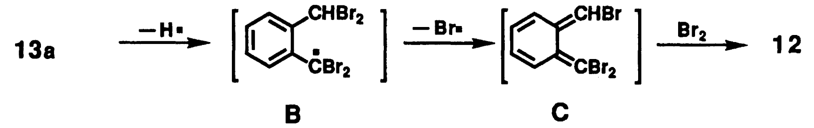
a; R=H, b; R=MeO, c; R=Br

Scheme 3.

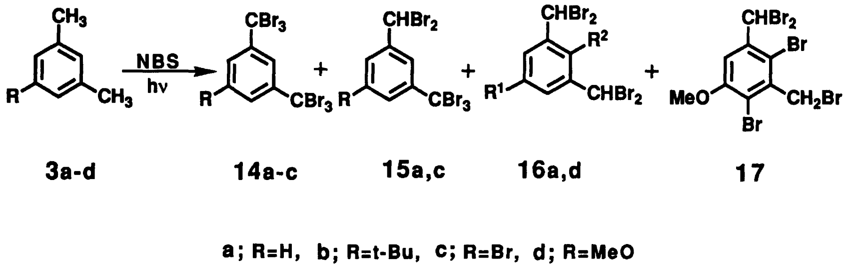
Table 2. Bromination$^{a,b)}$ of Dimethylbenzenes **2**—**4** and Trimethylbenzenes **5**—**6**

Arene	Solvent	Products, Yield$^{c)}$ (%)	Arene	Solvent	Products, Yield$^{c)}$ (%)
2a	CCl_4	**12** 71	**3a**	CCl_4	**14a**$^{d)}$ 64
	Benz$^{e)}$	**12** 55, **13a**$^{f)}$ 10		Benz	**14a** 67 **15a** 10
	dry Benz	**12** 60, **13a** 8		dry Benz	**14a** 79 **15a** 8
	CH_2Cl_2	**12** 6, **13a** 72		CH_2Cl_2	**14a** 13, **15a** 30, **16a**$^{f)}$ 29
2b	CCl_4	**13b** 80	**3b**	CCl_4	**14b** 85
	Benz	**13b** 82	**3c**	CCl_4	**14c** 76
2c	CCl_4	**13c** 55		Benz	**14c** 51, **15c** 23
	Benz	**13c** 58	**3d**	CCl_4	**16d** 79, **17** 9
				Benz	**16d** 72, **17** 10
			3e	CCl_4	**16e** 67
4a	CCl_4	**18**$^{d)}$ 62	**3f**	CCl_4	**16f** 61
	Benz	**18** 53, **19a** 11		Benz	**16f** 60
4b	CCl_4	**9i**+**10i** 72	**3g**	CCl_4	**16g** 66
	Benz	**9i**+**10i** 30, **19b** 10, **20** 29		Benz	**16g** 63
5	CCl_4	**21** 79	**6**	CCl_4	**23** 77
	Benz	**21** 51, **22** 24		Benz	**23** 74

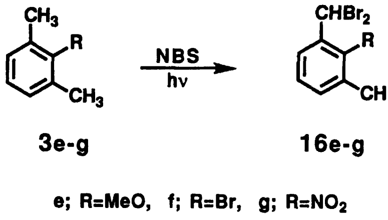
a) Bromination of **2**—**4** was carried out for 19 h using 6.4 equivalents of NBS, while 9.6 equivalents of NBS was used in the bromination of **5**—**6** for 20 h. b) Ten milligrams of AIBN was used for every 0.01 mol of the substrate **2**—**4** and 15 mg of AIBN for every 0.01 mol of **5**—**6**. c) Isolated yields are shown. d) B. F. Malicheko, G. I. Alyab'eva, and V. F. Kulik, *Zh. Obshch. Khim.*, **37**, 1626 (1967); *Chem. Abstr.*, **68**, 12580f (1968). e) Benz means benzene. f) M. Karfanto and N. Soyel, *Bull. Soc. Chim. Fr.*, **9**, 2966 (1966); *Chem. Abstr.*, **66**, 28720w (1967).



Scheme 4.



Scheme 5.

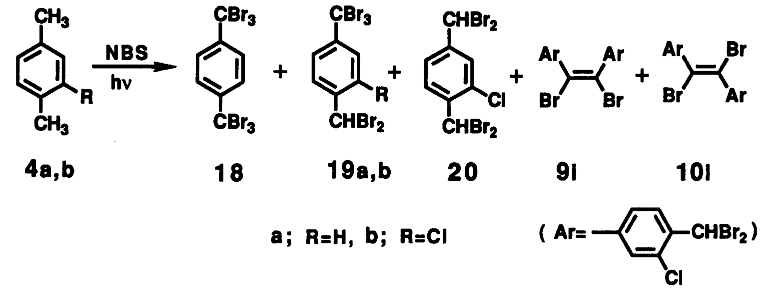


Scheme 6.

tetrabromide **13a**, the former being the major product.

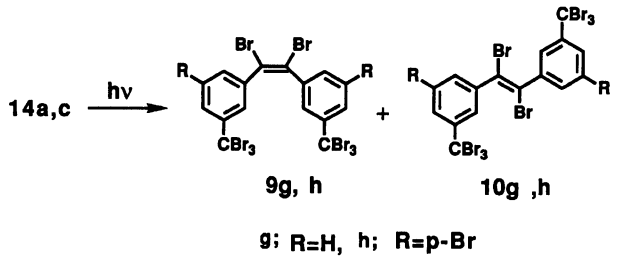
Formation of pentabromide **12** from **2a** was unexpected, since the substituents on the ortho-position of methylbenzenes **1** obstructed the introduction of the third bromo atom into the dibromomethyl group of **7d**—**f**. Contrary to **2a**, 3-methoxy-*o*-xylene (**2b**) and the 3-bromo derivative **2c** selectively gave the corresponding tetrabromides **13b** and **13c**. The formation pathway of **12** is tentatively proposed as follows (Scheme 4). Any radical species in the reaction mixture may abstract a hydrogen atom from **13a**, giving the dibromomethyl radical **B**. By extrusion of a bromo radical, **B** produces an *o*-quinodimethane intermediate **C**. Bromine formed by the reaction of a bromo radical with NBS adds on **C**, giving **12**. Formation of the corresponding *o*-quinodimethanes from **13b** and **13c** might be unfavorable because of the steric repulsions between substituents on 3-position and the exo-methylene moiety on 2-position.

m-Xylene (**3a**) gave hexabromide **14a** as a sole product in carbon tetrachloride, a mixture of **14a** and penta-



Scheme 7.

bromide **15a**, of which the former is predominant, in benzene, and **14a**, **15a**, and tetrabromide **16a** in dichloromethane. As expected, 5-*t*-butyl-*m*-xylene (**3b**) and the 5-bromo derivative **3c** selectively gave the corresponding hexabromide **14b** and **14c**, in the bromination using carbon tetrachloride as a solvent. The bromination of **3c** in benzene afforded **15b** as a by-product. Hexabromides **14a** and **14c** gave the expected stilbenes, **9g** and **10g**, and **9h** and **10h**, respectively, as a mixture of (*Z*)- and (*E*)-isomers on irradiation in the presence of AIBN (Eq. 3).

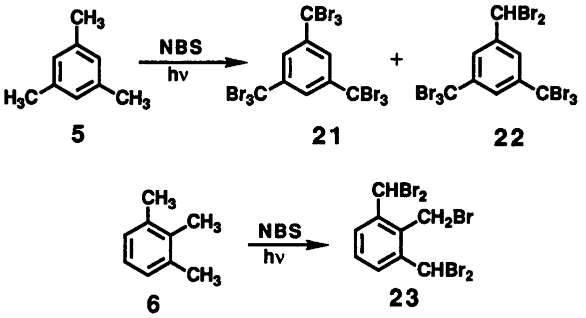


(3)

Ring-bromination took place during the bromination of 5-methoxy-*m*-xylene (**3d**) due to the enhanced electron density of the 2-position of the benzene ring and tetrabromide **16d** was produced in 72—79% yield, together with **17** in 9—10% yield. Substituents such as a methoxyl, bromo, or nitro group at the 2-position in **3e**—**g** deterred the tribromination as expected, giving tetrabromides **16e**—**g**. The ring-bromination of the 2-methoxy derivative **3e** looks sterically more favored than **3c**, but **3e** afforded none of the ring-brominated products, probably for electronic reasons.

The bromination of *p*-xylene (**4a**) selectively gave hexabromide **18** in carbon tetrachloride. Pentabromide **19a** was formed as a by-product in the reaction using benzene as a solvent. A mixture of tetrabromide **20**, pentabromide **19b**, and dibromostilbenes **9i** and **10i** was produced in the bromination of 2-chloro derivative **4b**. The corresponding hexabromide was not given, due to steric hindrance of the chloro substituent at the ortho position.

Bromination of Trimethylbenzenes 5—6. The formation of unstable perbromide in photochemical NBS-bromination of 2,4,6-trimethylpyridine has been reported.[5)]



Scheme 8.

Expectedly all three methy groups of 1,3,5-trimethylbenzene (**5**) were tribrominated, giving 1,3,5-tris(tribromomethyl)benzene **21** in 79% yield in carbon tetrachloride. Octabromide **22** was formed in 24% yield as a by-product in benzene, together with 51% of **21**. On the other hand, the central methyl group was only monobrominated and two methyl groups on both sides were dibrominated in the bromination of sterically congested 1,2,3-trimethylbenzene (**6**) and 2,6-bis(dibromomethyl)benzyl bromide (**23**) was obtained as the sole product (74—77% yield) (Scheme 8 and Table 2).

Conclusion. Methyl substituents of benzenes can be tribrominated using NBS with irradiation of a tungsten lamp in carbon tetrachloride or benzene under reflux, when there is no ortho substituent present; independent of their electronic properties, substituents on the ortho position deterred the tribromination.

Experimental

General. 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 JEOL GSX-270 using TMS as an internal standard in $CDCl_3$ unless otherwise stated. The electronic spectra were measured on a Hitachi 220A spectrophotometer in cyclohexane. The mass spectra were obtained on a JEOL JMS-01SG-2 mass spectrometer at 75 eV using a direct inlet system.

Photobromination of Methylbenzenes. General Procedure. A mixture of a methylbenzene **1**—**6**, NBS, and AIBN in a solvent was irradiated with a tungsten lamp (Nikko Electron Co., Ltd., RF-110 V/500 WH) without external cooling while stirring for the time given in Tables 1 and 2. Then, succinimide was filtered off and dilute aqueous sodium hydrogen sulfite was added to the filtrate. Organic layer was separated and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel (Wako gel), giving the products. Compounds **7a,d,f—i**, **8a—f**, **9a**, **c—i**, **10a**, **c—i**, **12**, **13a—c**, **14a—c**, **15a,c**, **16a,d,f—g**, **17**, **18**, **19a,b**, **20**, **21**, **22**, and **23** were eluted with hexane and **16e** with hexane–benzene (2:1).

Physical and spectral properties of new compounds are given below.

1-Bromo-3-(tribromomethyl)benzene (8e): Colorless oil; IR (NaCl) 1553, 1469, 1175, 878, 785, 733, and 696 cm^{-1}; ^{1}H NMR $\delta=7.26$ (1H, dd, $J=8.3$ and 7.9 Hz), 7.46 (1H, d, $J=7.9$ Hz), 7.92 (1H, d, $J=8.3$ Hz), and 8.14 (1H, s); ^{13}C NMR $\delta=38.04$, 121.68, 124.53, 129.99, 132.59, 143.61, and 148.01; MS m/z (rel intensity) 412 (M^+; 1), 410 (M^+; 4), 408 (M^+; 6), 406 (M^+; 4), 404 (M^+; 1), 331 (32), 329 (98), 327 (100), and 325 (34). Found: C, 20.72; H, 1.12%. Calcd for $C_7H_4Br_4$: C, 20.62; H, 0.99%.

(*Z*)-α,β,4,4′-Tetrabromostilbene (9c): Colorless needles (hexane); mp 153—155 °C; ^{1}H NMR $\delta=7.04$ (4H, d, $J=8.9$ Hz) and 7.31 (4H, d, $J=8.9$ Hz); UV λ_{max} 245 (ε 19100) and 305 (7760) nm; MS m/z (rel intensity) 500 (M^+; 9), 498 (M^+; 36), 496 (M^+; 56), 494 (M^+; 38), 492 (M^+; 10), and 336 (100). Found: C, 33.94; H, 1.98%. Calcd for $C_{14}H_8Br_4$: C, 33.91; H, 1.63%.

(*E*)-α,β,4,4′-Tetrabromostilbene (10c): Colorless prisms (benzene); mp 240—241 °C; ^{1}H NMR $\delta=7.39$ (4H, d, $J=8.6$ Hz) and 7.57 (4H, d, $J=8.6$ Hz); UV λ_{max} 255 (ε 19100) and 290 (7760) nm; MS m/z (rel intensity) 500 (M^+; 9), 498 (M^+; 36), 496 (M^+; 56), 494 (M^+; 38), 492 (M^+; 10), and 336 (100). Found: C, 33.98; H, 1.61%. Calcd for $C_{14}H_8Br_4$: C, 33.91; H, 1.63%.

A Mixture (56:44) of (*Z*)- and (*E*)-α,β-Dibromo-4,4′-dinitrostilbene (9d and 10d): Yellow crystalline powder (benzene); mp 155—76 °C; ^{1}H NMR $\delta=7.36$ (0.56×4H, d, $J=8.9$ Hz), 7.72 (0.44×4H, d, $J=8.9$ Hz), 8.06 (0.56×4H, d, $J=8.9$ Hz), and 8.32 (0.44×4H, d, $J=8.9$ Hz); MS m/z (rel intensity) 430 (M^+; 10), 428 (M^+; 19), 426 (M^+; 10), 268 (100). Found: C, 39.58; H, 2.00; N, 6.28%. Calcd for $C_{14}H_8Br_2N_2O_4$: C, 39.26; H, 1.88; N, 6.54%.

A Mixture (92:8) of (*Z*)- and (*E*)-α,β,3,3′-Tetrabromostilbene (9e and 10e): Colorless needles (hexane); mp 138—40 °C and 178—80 °C; ^{1}H NMR $\delta=$ 7.04—7.08 (0.08×3H, m), 7.25 (0.92×1H, t, $J=7.9$ Hz), 7.42—7.53 (0.92×2H, m), 7.65 (0.92×1H, t, $J=2.2$ Hz); and 7.73 (0.08×1H, s); MS m/z (rel intensity) 500 (M^+; 9), 498 (M^+; 35), 496 (M^+; 56), 494 (M^+; 38), 492 (M^+; 10), 417 (18), 415 (18), 338 (49), 336 (100), and 334 (54). Found: C, 33.87; H, 1.77%. Calcd for $C_{14}H_8Br_4$: C, 33.91; H, 1.63%.

(*Z*)-α,β-Dibromo-3,3′-dinitrostilbene (9f): Colorless prisms (benzene); mp 189—191 °C ; ^{1}H NMR $\delta=$ 7.36—7.42 (2H, m), 7.49—7.52 (2H, m), and 8.05—8.09 (4H, m); UV λ_{max} 245 (ε 24000) and 300 (6170) nm; MS m/z (rel intensity) 430 (M^+; 4), 428 (M^+; 38), 496 (M^+; 56), 494 (M^+; 38), 492 (M^+; 10), and 336 (100). Found: C, 39.13; H, 2.13; N, 6.47%. Calcd for $C_{14}H_8N_2O_4Br_2$: C, 39.28; H, 1.88; N, 6.54%.

(*E*)-α,β-Dibromo-3,3′-dinitrostilbene (10f): Yellow needles (benzene); mp 203—206 °C ; ^{1}H NMR $\delta=7.67$ (2H, t, $J=8.2$ Hz), 7.86—7.90 (2H, m), 8.26—8.31 (2H, m), and 8.43 (2H, t, $J=2.0$ Hz); UV λ_{max} 245 (ε 18200) and 290 (3980) nm; MS m/z (rel intensity) 430 (M^+; 36), 428 (M^+; 71), 426 (M^+; 38), and 268 (100). Found: C, 39.10; H, 1.60; N, 6.71%. Calcd for $C_{14}H_8N_2O_4Br_2$: C, 39.28; H, 1.88; N, 6.54%.

A Mixture (82:18) of (*Z*)- and (*E*)-α,β-Dibromo-3,3′-bis(tribromomethyl)stilbene (9g and 10g): Yellow crystalline powder (hexane); mp 135—144 °C ; ^{1}H NMR $\delta=7.26$—7.30 (0.82×2H, m), 7.47—7.55 (0.18×2H, m), 7.70—7.72 (0.82×1H, m), 7.74—7.78 (0.82×1H, m), 8.00—8.05 (0.18×1H, m), and 8.21—8.22 (0.18×1H, m); MS m/z (rel intensity) 843 (M^+; 8), 841 (M^+; 14), 839 (M^+; 19), 837 (M^+; 15), 835 (M^+; 8), 764 (19), 762 (61), 760 (100), 758 (99), 756 (60), and 754 (21). Found: C, 22.87; H, 1.12%. Calcd for $C_{16}H_6Br_8$: C, 22.89; H, 1.12%.

A Mixture (76:24) of (*Z*)- and (*E*)-α,β,3,3′-Tetrabromo-5,5′-bis(tribromomethyl)stilbene (9h and 10h): Yellow crystalline powder (hexane); mp 175—184 °C ; ^{1}H NMR $\delta=7.48$ (0.76×1H, dd, $J=1.8$ and 1.8 Hz), 7.58 (0.76×1H, dd, $J=1.8$ and 1.8 Hz), 7.66 (0.24×1H, dd, $J=1.8$ and 1.8 Hz), 7.91 (0.76×1H, dd, $J=1.8$ and 1.8 Hz), 8.10 (0.24×1H, dd, $J=1.8$ and 1.8 Hz), 8.14 (0.24×1H, dd, $J=1.8$ and 1.8 Hz), MS m/z (rel intensity) 1006 (M^+; 1), 1004 (M^+; 3), 1002 (M^+; 6), 1000 (M^+; 11), 998 (M^+; 14), 996 (M^+; 13), 994 (M^+; 8), 992 (M^+; 3), 990 (M^+; 1), 925 (7), 923 (27), 921 (64), 919 (95), 917 (100), 915 (69), 913 (29) and 911 (8). Found: C, 19.12; H, 0.68%. Calcd for $C_{16}H_6Br_{10}$: C, 19.27; H, 0.61%.

A Mixture (85:15) of (*Z*)- and (*E*)-α,β-Dibromo-3,3′-dichloro-4,4′-bis(dibromomethyl)stilbene (9i and 10i): Yellow crystalline powder (ethanol); mp 170—184 °C ; ^{1}H NMR $\delta=7.09$ (0.85×1H, s), 7.25 (0.15×1H, s), 7.48—7.53 (0.85×2H, m), 7.60—7.66 (0.15×2H, m), 8.03—8.07 (0.85×1H, m), and 8.31—8.34 (0.15×1H, m); MS m/z (rel intensity) 756 (M^+; 2), 754 (M^+; 5), 752 (M^+; 9), 750 (M^+; 14), 748 (M^+; 14), 746 (M^+; 8), 744 (M^+; 3), 675 (31), 673 (72), 671 (100), 669 (80), and 667 (34). Found: C, 25.46; H, 1.07%. Calcd for $C_{16}H_8Br_6Cl_2$: C, 25.60; H, 1.07%.

1-(Dibromomethyl)-2-(tribromomethyl)benzene (12): Pale yellow plates (hexane); mp 116—117 °C; IR 3062, 1471, 856, 784, and 653 cm^{-1}; ^{1}H NMR $\delta=7.30$ (1H, dd, $J=7.9$ and 7.6 Hz), 7.49 (1H, dd, $J=7.9$ and 7.6 Hz), 7.73 (1H, s), 7.94 (1H, d, $J=7.9$ Hz), and 8.16 (1H, d, $J=7.9$ Hz); ^{13}C NMR $\delta=36.21$, 38.01, 125.97, 128.68, 131.84, 134.99, 138.87, and 140.75; MS m/z (rel intensity) 504 (M^+; 5), 502 (M^+; 11), 500 (M^+; 12), 498 (M^+; 7), 425 (15), 423 (67), 421 (100), 419 (63), and 417 (17). Found: C, 19.43; H, 1.21%. Calcd for $C_8H_5Br_5$: C, 19.19; H, 1.01%.

1,2-Bis(dibromomethyl)-3-methoxybenzene (13b): Pale yellow needles (hexane); mp 144—146 °C; IR 1582, 1455, 1260, 1057, 828, 794, and 678 cm^{-1}; ^{1}H NMR $\delta=3.86$ (3H, s), 6.77 (1H, d, $J=8.2$ Hz), 7.38 (1H, dd, $J=8.2$ and 7.9 Hz), 7.54 (1H, s), 7.68 (1H, d, $J=7.9$ Hz), and 7.77 (1H, s); ^{13}C NMR $\delta=28.81$, 36.93, 56.37, 111.21, 124.25, 125.59, 131.46, 144.09, and 151.75; MS m/z (rel intensity) 455 (M^+; 2), 453 (M^+; 8), 451 (M^+; 13), 449 (M^+; 9), 447 (2), 374 (30), 372 (95), 370 (100), 368 (33). Found: C, 24.01; H, 1.81%. Calcd for $C_9H_8Br_4O$: C, 23.93; H, 1.79%.

1-Bromo-2,3-bis(dibromomethyl)benzene (13c): Colorless plates (hexane); mp 148—150 °C; IR 1449, 1229, 1137, 796, and 667 cm^{-1}; ^{1}H NMR $\delta=7.28$ (1H, dd, $J=8.3$ and 7.9 Hz), 7.46 (1H, s), 7.49 (1H, d, $J=8.3$ Hz), 7.72 (1H, s) and 8.06 (1H, d, $J=7.9$ Hz), ^{13}C NMR $\delta=35.10$, 36.71, 119.01, 131.75, 133.53, 133.56, 133.87, and 145.00; MS *m/z* (rel intensity) 504 (M^+; 3), 502 (M^+; 5), 500 (M^+; 5), 498 (M^+; 2), 425 (18), 423 (68), 421 (100), 419 (74), and 417 (18). Found: C, 19.48; H, 1.21%. Calcd for $C_8H_5Br_5$: C, 19.19; H, 1.01%.

1-*t*-Butyl-3,5-bis(tribromomethyl)benzene (14b): Colorless needles (hexane); mp 116—118 °C; IR 2960, 1592, 1429, 1159, 980, and 696 cm^{-1}; ^{1}H NMR δ=1.44 (9H, s), 7.80 (2H, d, J=2.3 Hz), and 8.50 (1H, t, J=2.3 Hz); ^{13}C NMR δ=31.18, 35.19, 35.46, 122.10, 125.39, 146.20, and 151.54; MS *m/z* (rel intensity), 638 (M^+; 4), 636 (M^+; 4), 634 (M^+; 4), 632 (M^+; 2), 561 (10), 559 (46), 557 (98), 555 (100), 553 (50), and 551 (11). Found: C, 22.41; H, 1.87%. Calcd for $C_{12}H_{12}Br_6$: C, 22.67; H, 1.90%.

1-Bromo-3,5-bis(tribromomethyl)benzene (14c): Colorless prisms (hexane); mp 134—136 °C; IR 1560, 1416, 1205, 1150, 1121, and 689 cm^{-1}; ^{1}H NMR δ=8.10 (2H, d, J=2.0 Hz) and 8.58 (1H, t, J=2.0 Hz); ^{13}C NMR δ=32.13, 121.64, 123.97, 131.02 and 148.28; MS *m/z* (rel intensity) 664 (M^+; 4), 662 (M^+; 11), 660 (M^+; 24), 658 (M^+; 21), 656 (M^+; 18), 654 (6), 585 (6), 583 (32), 581 (78), 579 (100), 577 (82), 575 (34), and 573 (6). Found: C, 14.56; H, 0.53%. Calcd for $C_8H_3Br_7$: C, 14.59; H, 0.46%.

1-(Dibromomethyl)-3-(tribromomethyl)benzene (15a): Pale yellow needles (hexane); mp 49—50 °C; IR 1481, 1429, 784, 725, and 691 cm^{-1}; ^{1}H NMR δ=6.68 (1H, s), 7.43 (1H, t, J=7.9 Hz), 7.60 (1H, d, J=7.9 Hz), 7.97 (1H, d, J=7.9 Hz), and 8.16 (1H, s); ^{13}C NMR δ=34.45, 39.55, 124.33, 127.89, 128.46, 128.72, 141.76, and 147.08; MS *m/z* (rel intensity) 502 (M^+; 0.9), 500 (M^+; 0.9), 425 (16), 423 (63), 421 (100), 419 (66), and 417 (17). Found: C, 19.04; H, 1.01%. Calcd for $C_8H_5Br_5$: C, 19.12; H, 1.01%.

1-Bromo-3-(dibromomethyl)-5-(tribromomethyl)benzene (15c): Colorless oil; IR (NaCl) 3004, 1657, 1419, 1147, 972, 873, 732, and 696 cm^{-1}; ^{1}H NMR δ=6.60 (1H, s), 7.74 (1H, dd J=1.5 and 1.5 Hz), 8.07 (1H, dd J=2.0 and 1.6 Hz), and 8.10 (1H, dd J=2.0 and 1.6 Hz); ^{13}C NMR δ=32.09, 37.86, 122.05, 123.27, 130.78, 131.43, 143.27, and 148.48; MS *m/z* (rel intensity) 584 (M^+; 1), 582 (M^+; 3), 580 (M^+; 4), 578 (M^+; 3), 576 (M^+; 2), 574 (M^+; 1), 505 (9), 503 (47), 501 (96), 499 (100), 497 (51), and 495 (10). Found: C, 16.88; H, 0.84%. Calcd for $C_8H_4Br_6$: C, 16.58; H, 0.70%.

2-Bromo-1,3-bis(dibromomethyl)-5-methyoxybenzene (16d): Colorless crystalline powder (hexane); mp 118—120 °C; IR 1592, 1288, 1017, 978, 887, and 734 cm^{-1}; ^{1}H NMR δ=3.92 (3H, s), 7.10 (2H, s), and 7.62 (2H, s); ^{13}C NMR δ=39.26, 55.88, 107.41, 118.35, 141.58, and 159.58; MS *m/z* (rel intensity) 536 (M^+; 2), 534 (M^+; 10), 532(M^+; 20), 530(M^+; 21), 528(M^+; 10), 526(M^+; 2), 455 (16), 453 (66), 451 (100), 449 (68), and 447 (17). Found: C, 20.36; H, 1.33%. Calcd for $C_9H_7Br_5O$: C, 20.36; H, 1.33%.

1,3-Bis(dibromomethyl)-2-methoxybenzene (16e): Colorless prisms (hexane); mp 122—124 °C IR 1548, 1454, 1251, 820, and 757 cm^{-1}; ^{1}H NMR δ=3.95 (3H, s), 7.01 (2H, s), and 7.34 (1H, t, J=7.9 Hz), and 7.90 (2H, d, J=7.9 Hz); ^{13}C NMR δ=33.03, 62.59, 126.31, 132.50, 135.47, and 147.98; MS *m/z* (rel intensity) 454 (M^+; 7) 452 (M^+; 11), 450 (M^+; 20), 448 (M^+; 13), 375 (30), 373 (100), and 369 (32). Found: C, 24.01; H, 1.81%. Calcd for $C_9H_8Br_4O$: C, 23.93; H, 1.79%.

2-Bromo-1,3-bis(dibromomethyl)benzene (16f): Pale yellow plates (hexane); mp 148—149 °C IR 1420, 1149, 1201, 1021, 937, and 721 cm^{-1}; ^{1}H NMR δ=7.13 (2H, s), 7.53 (1H, t, J=7.9 Hz), and 8.05 (2H, d, J=7.9 Hz); ^{13}C NMR δ=39.21, 117.07, 129.73, 132.44, and 140.70; MS *m/z* (rel intensity) 506 (M^+; 0.3), 504 (M^+; 1), 502 (M^+; 3), 500 (M^+; 2), 498 (M^+; 1), 496 (M^+; 0.3), 425 (16), 423 (65), 421 (100), and 419 (70). Found: C, 19.07; H, 1.11%. Calcd for $C_8H_9Br_5$: C, 19.19; H, 1.01%.

1,3-Bis(dibromomethyl)-2-nitrobenzene (16g): Pale yellow needles (hexane); mp 132—134 °C IR 1581, 1461, 1138, 853, and 715 cm^{-1}; ^{1}H NMR δ=6.65 (2H, s), 7.74 (1H, t, J=8.3 Hz), and 8.14 (2H, d, J=8.3 Hz); ^{13}C NMR δ=31.32, 131.81, 131.97, 132.81, and 141.13; MS *m/z* (rel intensity) 471 (M^+; 2), 469 (M^+; 8), 467 (M^+; 11), 465 (M^+; 8), 463 (M^+; 2), 390 (33), 388 (98), 386 (100), and 384 (34). Found: C, 20.55; H, 1.18; N, 2.93%. Calcd for $C_8H_5Br_4NO_2$: C, 20.59; H, 1.07; N, 3.00%.

2,4-Dibromo-3-bromomethyl-1-(dibromomethyl)-5-methoxybenzene (17): Colorless crystalline powder (hexane); mp 125—126 °C IR 1571, 1454, 1130, 1053, 989, 881, 739, and 679 cm^{-1}; ^{1}H NMR δ=4.00 (3H, s), 4.89 (2H, s), 7.14 (1H, s) and 7.54 (1H, s); ^{13}C NMR δ=34.50, 39.77, 56.82, 112.78, 113.33, 117.47, 137.45, 141.02 and 156.17; MS *m/z* (rel intensity) 536 (M^+; 3), 534 (M^+; 12), 532 (M^+; 25), 530 (M^+; 26), 528 (13), 526 (3), 455 (16), 453 (65), 451 (100), 449 (65), 447 (17). Found: C, 20.30; H, 1.34%. Calcd for $C_9H_7Br_5O$: C, 20.36; H, 1.33%.

1-(Dibromomethyl)-4-(tribromomethyl)benzene (19a): Colorless needles (hexane); mp 184—186 °C; IR 1406, 1149, 797, and 731 cm^{-1}; ^{1}H NMR δ=6.65 (1H, s), 7.60 (2H, d, J=8.6 Hz), and 8.02 (2H, d, J=8.6 Hz); ^{13}C NMR δ=34.38, 39.05, 126.27, 126.95, 143.34, and 147.89; MS *m/z* (rel intensity) 502 (M^+; 1), 500 (M^+; 1), 498 (M^+; 0.6), 425 (16), 423 (62), 421 (100), 419 (66), and 417 (18). Found: C, 19.42; H, 1.17%. Calcd for $C_8H_5Br_5$: C, 19.19; H, 1.01%.

2-Chloro-1-(dibromomethyl)-4-(tribromomethyl)benzene (19b): Colorless oil; IR (NaCl) 3026, 1598, 1555, 1387, 1228, 1149, 1049, 804, and 747 cm^{-1}; ^{1}H NMR δ=7.03 (1H, s), 7.95—8.03 (3H, m); ^{13}C NMR δ=32.26, 35.09, 126.18, 127.31, 129.16, 130.60, 140.12, 148.77; MS *m/z* (rel intensity) 538 (M^+; 1), 536 (M^+; 2), 534 (M^+; 1), 532 (M^+; 1), 461 (4), 459 (30), 457 (80), 455 (100), 453 (59), and 451 (15). Found: C, 18.15; H, 0.93%. Calcd for $C_8H_4Br_5Cl$: C, 17.96; H, 0.75%.

2-Chloro-1,4-bis(dibromomethyl)benzene (20): Colorless oil; IR (NaCl) 3028, 1602, 1486, 1400, 1232, 1147, 1049, and 797 cm^{-1}; ^{1}H NMR δ=6.56 (1H, s), 7.00 (1H, s), 7.54 (1H, d, J=2.0 Hz), 7.57 (1H, dd, J=8.6 and 2.0 Hz), and 7.99 (1H, d, J=8.6 Hz); ^{13}C NMR δ=35.45, 37.95, 126.09, 127.44, 129.77, 131.32, 139.98, and 144.24; MS *m/z* (rel intensity) 460 (M^+; 1), 458 (M^+; 4), 456 (M^+; 5), 454 (M^+; 3), 452 (M^+; 2), 381 (8), 379 (48), 377 (100), 375 (86), 373 (27), and 451 (15). Found: 20.96; H, 1.20%. Calcd for $C_8H_5Br_4Cl$: C, 21.06; H, 1.10%.

1,3,5-Tris(tribromomethyl)benzene (21): Colorless needles (hexane); mp 190—192 °C IR 1586, 1432, 1413, 1159, 984, and 714 cm^{-1}; ^{1}H NMR δ=8.66 (3H, s); ^{13}C NMR δ=32.58, 126.14, 140.12, and 148.77; MS *m/z* (rel intensity) 757 (11), 755 (38), 753 (80), 751 (100), 749 (83), 747 (43) and 745 (13). Found: C, 12.90; H, 0.58%. Calcd for $C_9H_3Br_9$: C, 13.04; H, 0.40%.

5-(Dibromomethyl)-1,3-bis(tribromomethyl)benzene (22): White powder (hexane); mp 88—90 °C; IR 1409, 1142, 974, 757, and 690 cm^{-1}; ^{1}H NMR δ=6.72 (1H, s), 8.19 (2H, d, J=1.7 Hz), 8.63 (1H, t, J=1.7 Hz); ^{13}C NMR δ=32.70, 38.29, 126.07, 126.18, 141.96, and 147.16; MS m/z (rel intensity) 676 (19), 674 (57), 672 (96), 670 (100), 668 (61), and 666 (21). Found: C, 14.65; H, 0.69%. Calcd for $C_9H_4Br_8$: C, 14.41; H, 0.54%.

2-Bromomethyl-1,3-bis(dibromomethyl)benzene (23): Pale yellow needles (hexane); mp 111—112 °C IR 1453, 1241, 1137, 752, and 630 cm^{-1}; ^{1}H NMR δ=4.69 (2H, s), 7.01 (2H, s), 7.49 (1H, t, J=7.9 Hz), and 7.94 (2H, d, J=7.9 Hz); ^{13}C NMR δ=22.54, 35.54, 127.40, 130.28, 131.68, and 140.45; MS m/z (rel intensity) 516 (M$^+$; 3), 514 (M$^+$; 3), 439 (18), 437 (64), 435 (100), 433 (67), 431 (17). Found: C, 21.29; H, 1.41%. Calcd for $C_9H_7Br_5$: C, 21.00; H, 1.37%;

Ethyl Benzoate 11 from the Bromination Mixture of 1. Typical Procedure. Compound **1b** was tribrominated under the conditions given in Table 1. Succinimide was filtered and ethanol was added to the filtrate. The mixture was stirred at room temperature for 5 h and evaporated under reduced pressure to leave a residue which was chromatographed. Ester **11b** was eluted with hexane–benzene (2:1).

Similarly **11f** was obtained from the bromination mixture of **1m**.

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