mixture was boiled under reflux for 2 hr. The mixture was cooled and poured onto crushed ice. The resulting solution was extracted with chloroform; the chloroform extract was washed with aqueous sodium bicarbonate and water. Removal of the solvent from the dried extract gave **25** as a light brown liquid (0.44 g, 62%), which on evaporative distillation at 30° (0.05 mm) gave colorless needles, mp 34–36°.

Treatment of 24 with Base.—The unsaturated acid **24** (140 mg) was stirred with aqueous 15% sodium hydroxide (15 ml) for 3 days. The mixture was cooled, acidified with 10% hydrochloric acid, and saturated with ammonium sulfate. The solution was extracted with ethyl acetate. Removal of the solvent from the dried extract gave a colorless, viscous oil (135 mg). This was triturated with carbon tetrachloride, when a crystalline white solid (90 mg, 65%) was obtained, which was identified as **24** by mixture melting point. Removal of carbon tetrachloride from the solution gave a light brown, viscous oil (24 mg) whose nmr spectrum showed no vinylic proton signal and whose infrared spectrum (CCl_4) showed no band at 5.60 μ.

Base-Catalyzed Hydrolysis of 17. Formation of 27.—The dilactone **17** (1.5 g, 0.0045 mol) was stirred under nitrogen with saturated ethanolic sodium hydroxide (90 ml) for 15 min, when a faint yellow solution was obtained. The solution was cooled in ice and acidified (pH 2) with cold 10% hydrochloric acid. The solution was saturated with ammonium sulfate and extracted with ethyl acetate. Removal of the solvent from the dried extract gave a light brown, thick oil (1.36 g) that showed eight overlapping spots on a silica tlc plate when developed with chloroform and methanol (9:1). It was chromatographed on silica gel (45 g) in benzene and eluted with benzene containing increasing amounts of ether. Early eluates with 10% ether in benzene afforded a thick oil that on crystallization from benzene–petroleum ether afforded brown crystals (17 mg). Recrystallization from chloroform–cyclohexane afforded **27** as colorless needles: mp 192–194°; $\lambda_{max}^{CHCl_3}$ 2.8–4.1 (complex), 5.75, 5.88 (sh) μ; $\delta^{CF_3CO_2H}$ 0.8–1.5 (m, 12), 1.6–2.3 (m, 8), 2.8–4.3 (m, 4).

Anal. Calcd for $C_{18}H_{26}O_7$: C, 61.02; H, 7.34. Found: C, 60.88; H, 7.39.

Elution with 25% ether in benzene gave a thick oil that on crystallization from cyclohexane–chloroform afforded colorless crystals (210 mg), mp 153–157° dec. Five recrystallizations gave microcrystals: mp 181–182° dec; λ_{max}^{KBr} 2.88, 3.0–4.2 (complex) 5.82, 5.91, 6.09 μ; λ_{max}^{EtOH} 212 mμ (ϵ 7020), 230 mμ (sh, ϵ 5700); $\delta^{CF_3CO_2H}$ 0.83–1.40 (m, 12), 1.40–2.66 (m, 8), 3.93–4.33 (m, 3), 6.24 (br s, 1).

Anal. Calcd for $C_{18}H_{28}O_8$: C, 58.06; H, 7.31. Found: C, 57.89; H, 7.35.

Registry No.—**2**, 19034-31-2; **3**, 14774-14-2; **4**, 21559-91-1; **7**, 21543-79-3; **7** (2,4-dinitrophenylhydrazone), 21543-80-6; **8**, 19052-75-6; **9**, 21588-61-4; **10**, 21559-92-2; **12**, 21559-93-3; **13a**, 21559-94-4; **13b**, 21559-95-5; **14**, 21559-96-6; **16**, 21559-97-7; **17**, 21559-98-8; **18**, 21559-99-9; **19**, 21560-00-9; **24**, 21543-82-8; **25**, 1575-44-6; **27**, 21588-62-5; 3-hydroxy-3-(methoxymethyl)pentanoic acid, 21543-84-0; 3-hydroxy-3-(methoxymethyl)pentanoic acid ethyl ester, 21543-85-1.

Acknowledgment.—We thank the National Research Council of Canada for generous support of part of this work.

Photodimeric Cage Compounds. III. The Reaction of the Photodimer of 2,6-Dimethyl-4-pyrone with Bromine[1]

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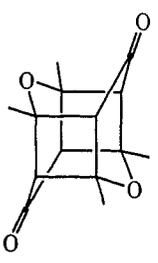
Reaction of the cage photodimer of 2,6-dimethyl-4-pyrone with liquid bromine gives tetrabromo, hexabromo, heptabromo, and octabromo substitution products of the *seco*-dimer **3**. Treatment of these products with sulfuric acid cleaves the remaining cyclobutane ring and gives dibromo, tribromo, and tetrabromo substitution products of 2,6-dimethyl-4-pyrone.

Irradiation of 2,6-dimethyl-4-pyrone gives the cage photodimer **1**.[3] This is resistant to bromine under mild conditions, but reacts vigorously with excess liquid bromine to give four products: A, $C_{14}H_{12}Br_4O_4$; B, $C_{14}H_{10}Br_6O_4$; C, $C_{14}H_9Br_7O_4$; and D, $C_{14}H_8Br_8O_4$.



1

The hexabromo compound B is assigned structure **2** on the basis of its origin from **1** and its spectra. It shows in its infrared spectrum (Table I) bands characteristic of an α,β-unsaturated carbonyl system. This spectrum may be compared with that of the *seco*-dimer **3**, which is obtained by pyrolysis or acid treatment of **1**.[3,4] The hypsochromic shift of the carbonyl stretching band is readily interpretable in terms of the attachment of a bromine atom to the α-ethylenic carbon atom,[5] as is the bathochromic shift of the ethylenic stretching band.[6] The ultraviolet spectrum of compound B (Table I) corroborates the presence of one or more α,β-unsaturated carbonyl systems in the molecule. Its relationship to the ultraviolet spectrum of **3** is in good accord with the assignment of structure **2** to compound B, since it is known that α-bromo substituents on the ethylenic double bond of an α,β-unsaturated carbonyl system give rise to appreciable bathochromic[7] and hypochromic[8] shifts of the $\pi \rightarrow \pi^*$ band. The signals in the nmr spectrum of compound B can be

(1) Paper II: P. Yates, E. S. Hand, P. Singh, S. K. Roy, and I. W. J. Still, *J. Org. Chem.* **34**, 4046 (1969).

(2) Commonwealth Scholar, 1963–1966.

(3) P. Yates and M. J. Jorgenson, *J. Amer. Chem. Soc.*, **85**, 2956 (1963); **80**, 6150 (1958).

(4) D. J. MacGregor, Ph.D. Thesis, University of Toronto, 1967.

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 137.

(6) R. N. Jones and C. Sandorfy "Chemical Applications of Spectroscopy," W. West, Ed. ("Technique of Organic Chemistry," A. Weissberger, Ed., Vol. IX), Interscience Publishers, Inc., New York, N. Y., 1956, p 371.

(7) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, New York, N. Y., 1964, p 58.

(8) *Cf.* A. T. Nielsen, *J. Org. Chem.*, **22**, 1539 (1957).

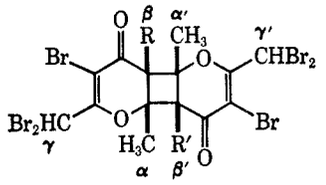
TABLE I

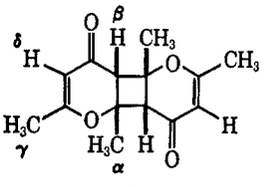
INFRARED AND ULTRAVIOLET SPECTRA OF THE BROMINATION PRODUCTS FROM THE PHOTODIMER OF 2,6-DIMETHYL-4-PYRONE

Compound	$\lambda_{max}^{CHCl_3}$, μ	$\lambda_{max}^{CHCl_3}$, mμ (ε)
A (7)	5.95, 6.31	298 (17,700)
B (2)	5.94, 6.33	300 (17,000)
C (11)	5.93, 6.33	302 (16,000)
D (9)	5.91, 6.31	306 (12,000)
3	6.04 (br),[a] 6.18	266 (21,900)[b]

[a] In some spectra this band was resolved into two peaks at 6.02 and 6.05μ. [b] In ethanol.

assigned as indicated in Table II. This spectrum may also be compared with that of **3**; the magnitude of the





3

2, R, R′ = H
9, R, R′ = Br
11, R = H; R′ = Br

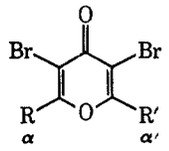
downfield shift of the signal associated with the C_γ protons of **2** in relation to that for the C_γ protons of **3** is in accord with expectation for the substitution of two bromine atoms on each C_γ.[9]

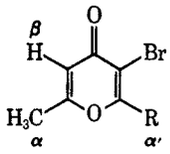
TABLE II

NMR SPECTRA OF THE BROMINATION PRODUCTS FROM THE PHOTODIMER OF 2,6-DIMETHYL-4-PYRONE

		δ^{CDCl_3}, ppm		
Compound	α,α′	β,β′	γ,γ′	δ
A (7)	1.69 (s, 6 H)	3.32 (s, 2 H)	4.16 (s, 4 H)	
B (2)	1.76 (s, 6 H)	3.40 (s, 2 H)	6.74 (s, 2 H)	
C (11)	1.82 (s, 3 H)	3.62 (s, 1 H)	6.70 (br s, 2 H)	
	1.90 (s, 3 H)			
D (9)	2.05 (s, 6 H)		6.68 (s, 2 H)	
3	1.70 (s, 6 H)	3.10 (s, 2 H)	1.93 (s, 6 H)	5.25 (s, 2 H)

Treatment of **2** with concentrated sulfuric acid gave a crystalline product, $C_7H_5Br_3O_2$. This was reduced by zinc and acetic acid to 2,6-dimethyl-4-pyrone in high yield. This observation and comparison of the compound's spectra with those of 2,6-dimethyl-4-pyrone and the model compounds **4**[10] and **5**[11] (Tables III and IV)





4, R, R′ = CH_3
5, R, R′ = CH_2Br
10, R = CH_3; R′ = $CHBr_2$

6, R = $CHBr_2$
8, R = CH_2Br

lead to formulation of the product as 3-bromo-2-dibromomethyl-6-methyl-4-pyrone (**6**). The formation of **6** from **2** is analogous to the formation of 2,6-dimethyl-4-pyrone from **3** by acid-catalyzed cleavage[3,4] and can be formulated as in Scheme I.

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p 59.

(10) Compound **4** was prepared by a modification of the method of L. L. Woods and P. A. Dix, *J. Org. Chem.*, **26**, 2588 (1961); it was shown to give 2,6-dimethyl-4-pyrone on reduction with zinc and acetic acid.

(11) Compound **5** was prepared by the method of J. N. Collie and L. Klein, *J. Chem. Soc.*, 2162 (1927).

SCHEME I

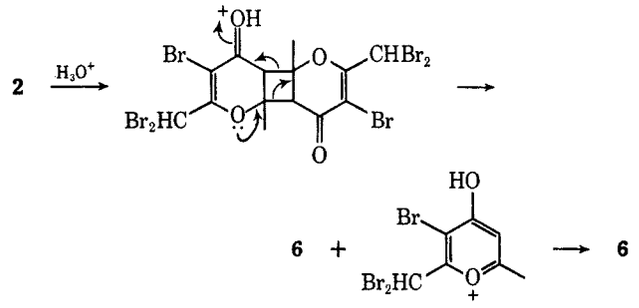


TABLE III

INFRARED AND ULTRAVIOLET SPECTRA OF 2,6-DIMETHYL-4-PYRONE AND ITS BROMINATED DERIVATIVES

4-Pyrone	$\lambda_{max}^{CHCl_3}$, μ	λ_{max}^{EtOH}, mμ (ε)
2,6-Dimethyl	5.99, 6.21	246 (14,700)
3,5-Dibromo-2,6-dimethyl (**4**)	6.10,[a] 6.13	230 (5800)[b]
		263 (5500)
3,5-Dibromo-2,6-bis(bromomethyl) (**5**)	6.01, 6.17	236 (11,650)
		277 (6500)
3-Bromo-2-dibromomethyl-6-methyl (**6**)	6.03, 6.11[a]	224 (7100)[b]
		266 (7900)
3-Bromo-2-bromomethyl-6-methyl (**8**)	6.05, 6.11[c]	222 (7700)[b]
		264 (9000)
3,5-Dibromo-2-dibromomethyl-6-methyl (**10**)	6.04, 6.17	268 (6900)

[a] Shoulder. [b] Inflection. [c] Weak.

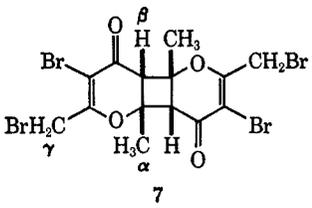
TABLE IV

NMR SPECTRA OF 2,6-DIMETHYL-4-PYRONE AND ITS BROMINATED DERIVATIVES[a]

	δ^{CDCl_3}, ppm		
4-Pyrone	α	α′	β
2,6-Dimethyl	2.25 (6 H)		6.06 (2 H)
3,5-Dibromo-2,6-dimethyl (**4**)	2.50		
3,5-Dibromo-2,6-bis-(bromomethyl) (**5**)	4.55		
3-Bromo-2-dibromomethyl-6-methyl (**6**)	2.40 (3 H)	6.95 (1 H)	6.22 (1 H)[b]
3-Bromo-2-bromomethyl-6-methyl (**8**)	2.32 (3 H)	4.48 (2 H)	6.20 (1 H)[b]
3,5-Dibromo-2-dibromomethyl-6-methyl (**10**)	2.68 (3 H)	6.97 (1 H)	

[a] All signals are singlets. [b] Broad.

The tetrabromo compound A was converted by treatment with bromine in chloroform to the hexabromo compound B (**2**). On the basis of this observation and its spectra (Tables I and II), it can be assigned structure **7**. On treatment with sulfuric acid it gave a crystalline product, $C_7H_6Br_2O_2$, which is considered to be 3-bromo-2-bromomethyl-6-methyl-4-pyrone (**8**); its spectra are given in Tables III and IV.



7

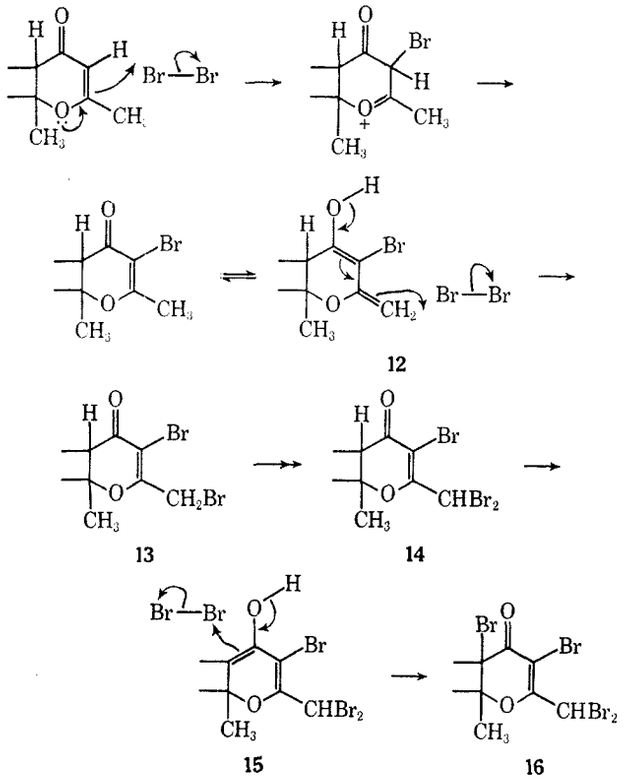
The octabromo compound D was obtained as one of the products when the hexabromo compound B (**2**) was brominated with bromine in chloroform. This

relationship and the spectra of D (Tables I and II) lead to its formulation as **9**. Cleavage with concentrated sulfuric acid gave a crystalline product, $C_7H_4Br_4O_2$, considered on the basis of its spectra (Tables III and IV) to be 3,5-dibromo-2-dibromomethyl-6-methyl-4-pyrone (**10**).

The heptabromo compound C was also obtained on bromination of the hexabromo compound B (**2**); on further bromination it gave the octabromo compound D (**9**). On treatment with sulfuric acid it was converted to the pyrones **6** and **10**. It can therefore be formulated as **11**, with which structure its spectra (Tables I and II) are in accord.

The bromination products A–D are considered to arise from the cage photodimer **1** *via* acid-catalyzed cleavage to give the *seco*-dimer **3** followed by bromination of this compound. It is counted unlikely that bromination of the intact cage compound would occur, due to steric inhibition of enolization. The formation of A–D from **3** is unexceptional and is considered to occur *via* routes of the type shown in Scheme II. Preferential enolization in the sense shown in **12** is expected because formation of the alternative enol would require

SCHEME II



introduction of the double bond in the less favorable bridgehead position. The same consideration is seen to apply in the case of the enolization of **13**, accounting for the formation of products of type **14**. However, enolization of **14** must occur toward the cyclobutane ring as in **15** to account for the formation of products of type **16**. This is not unexpected, since enolization of **14** in the opposite sense would introduce severe interaction between two of its bromine atoms.

Irradiation of compound B (**2**) in the solid state with a 450-W medium-pressure mercury arc lamp led to no change after 5 days. Irradiation of this compound or compound D (**9**) in solution gave dark brown, pungent oils from which no pure product was obtained. Similar results were obtained on irradiation of the pyrones **6** and **10**.

Experimental Section

Melting points were determined in capillary tubes with a Thomas-Hoover "Uni-Melt" apparatus and are uncorrected. Solutions in organic solvents were dried over anhydrous magnesium sulfate. Spectra are given in Tables I–IV.

Bromination of the Photodimer of 2,6-Dimethyl-4-pyrone (1). Formation of Compounds A–D (7, 2, 11, 9).—The photodimer **1** (2.88 g, 0.012 mol) was treated with liquid bromine (18.0 g, 0.112 mol) at room temperature. The reaction was exothermic and vigorous evolution of hydrogen bromide took place. After *ca.* 2 hr most of the bromine had evaporated or reacted, and the evolution of gas ceased. The bright orange solid product was washed with aqueous sodium sulfite, aqueous sodium bicarbonate, and water to give a light brown solid (7.24 g) that showed bands at 5.92 and 6.31 μ in its infrared spectrum. This solid was chromatographed on silica gel (250 g) in benzene and eluted with benzene containing increasing amounts of ether. The early eluates with 3% ether in benzene gave a crystalline solid that on recrystallization from benzene–petroleum ether (bp 30–60°) gave compound D as colorless crystals, mp 213–216° (635 mg), and the later eluates with this eluent gave a viscous oil that on crystallization from benzene–petroleum ether gave compound C as pale brown crystals, mp 201–204° dec (362 mg). The eluates with 4% ether in benzene gave a light brown viscous oil (3.5 g) that was rechromatographed on silica gel in benzene with elution with benzene containing 3% ether. Crystallization of the fractions from benzene and benzene–petroleum ether gave compound B as sparingly soluble colorless crystals, mp 219–223° dec (927 mg), together with D (119 mg) and C (523 mg). Eluates from the original chromatogram with 10% ether in benzene gave a semisolid material (3.7 g) and a light brown solid. The latter on crystallization from benzene–petroleum ether gave compound A, mp 170–175° (130 mg). The semisolid material was rechromatographed as before, and fractions were obtained that on crystallization from benzene and benzene–petroleum ether gave further amounts of compounds D (120 mg), C (303 mg), B (507 mg), and A (270 mg).

The crude **compound D** (874 mg, 9%) was recrystallized thrice from benzene–petroleum ether to give D (**9**) as colorless crystals, mp 214.5–216°.

Anal. Calcd for $C_{14}H_8Br_8O_4$: C, 19.09; H, 0.91; Br, 72.73. Found: C, 19.12; H, 0.89; Br, 73.07.

The crude **compound C** (1.188 g, 13%) was decolorized with Norit in benzene and recrystallized from benzene–petroleum ether to give C (**11**) as colorless crystals, mp 212–212.5° dec.

Anal. Calcd for $C_{14}H_9Br_7O_4$: C, 21.00; H, 1.13; Br, 69.87. Found: C, 21.05; H, 1.27; Br, 69.84.

The sparingly soluble crude **compound B** (1.434 g, 17%) was recrystallized twice from benzene to give B (**2**) as a white powder, mp 230–231° dec.

Anal. Calcd for $C_{14}H_{10}Br_6O_4$: C, 23.29; H, 1.40; Br, 66.44. Found: C, 23.60; H, 1.43; Br, 66.49.

The crude **compound A** (400 mg, 6%) was chromatographed on silica gel in benzene. Elution with benzene containing 5% ether afforded a colorless solid. This was crystallized from chloroform–petroleum ether to give A (**7**) as colorless crystals that turned black at 180–185° but did not melt below 300°.

Anal. Calcd for $C_{14}H_{12}Br_4O_4$: C, 29.79; H, 2.13; Br, 56.74. Found: C, 29.93; H, 2.14; Br, 56.80.

Treatment of 2 with Acid. Formation of 3-Bromo-2-dibromomethyl-6-methyl-4-pyrone (6).—The hexabromo compound **2** (580 mg, 0.805 mmol) was added to concentrated sulfuric acid (10 ml) that had been preheated on a steam bath for 15 min. The reaction mixture was heated for a further 15 min, when a brown solution was obtained. The solution was cooled and poured onto ice, and the resulting product was extracted with chloroform. The extract was washed with saturated aqueous sodium bicarbonate and water and dried. Removal of the solvent gave **6** as light brown crystals (450 mg, 78%). This was chromatographed on silica gel in benzene; elution with benzene containing 10% ether gave pale yellow crystals (350 mg). Decolorization with Norit and recrystallizations from cyclohexane gave **6** as shining, white needles, mp 114–115°.

Anal. Calcd for $C_7H_5Br_3O_2$: C, 23.67; H, 1.40; Br, 66.49. Found: C, 23.56; H, 1.41; Br, 66.34.

Reduction of 6 with Zinc and Acetic Acid. Formation of 2,6-Dimethyl-4-pyrone.—A solution of **6** (110 mg, 0.305 mmol) in glacial acetic acid (7 ml) and zinc powder (1.5 g) were heated under reflux for 4 hr. The reaction mixture was allowed to stand overnight and filtered. The filtrate was cooled and made alkaline (pH 8) with solid sodium bicarbonate. The solution was extracted with chloroform, and the extract was dried. Removal of the solvent gave 2,6-dimethyl-4-pyrone as needles (36 mg, 98%), mp 132.5–133.5°, after recrystallization from cyclohexane. This was identified by an undepressed mixture melting point with an authentic sample, and infrared and nmr spectral comparison.

Bromination of 2,6-Dimethyl-4-pyrone. Formation of 3,5-Dibromo-2,6-dimethyl-4-pyrone (4).—A modified version of the method of Woods and Dix[10] was used. Liquid bromine (33.0 g, 0.206 mol) was added to a solution of 2,6-dimethyl-4-pyrone (12.4 g, 0.100 mol) in trifluoroacetic acid (20 ml) in a round-bottomed flask fitted with an efficient reflux condenser. An exothermic reaction ensued, and hydrogen bromide was evolved. The reaction mixture was heated under reflux; after 2 hr it was cooled and poured onto crushed ice. The resulting mixture was allowed to stand for 2 days after which a viscous oil formed. This was taken up in chloroform, and the solution was washed thoroughly with aqueous 10% sodium sulfite, 10% hydrochloric acid, and water. The chloroform solution was dried and freed of solvent to give **4** as a pale yellow solid (12.0 g, 42%). After recrystallization from cyclohexane **4** was obtained as shining white needles, mp 164–165° (lit[10] mp 152°).

3,5-Dibromo-2,6-dimethyl-4-pyrone (**4**) was reduced quantitatively to 2,6-dimethyl-4-pyrone when heated under reflux for 4 hr with zinc and acetic acid as in the procedure described above for **6**.

Treatment of 7 with Bromine. Formation of 2.—A solution of bromine (100 mg, 0.62 mmol) in chloroform (10 ml) was added very slowly to a stirred solution of **7** (70 mg, 0.12 mmol) in chloroform (5 ml) over a period of 8 days, and the mixture was stirred for another 4 days. The solution was washed with aqueous 10% sodium sulfite and water, and dried over sodium sulfate. Removal of the solvent gave a white solid (50 mg) which was chromatographed on silica gel in benzene. Elution with 2% ether in benzene gave a solid (25 mg), that was identified as the hexabromo compound **2** by nmr and infrared spectral comparison. Recrystallization from benzene gave **2**, mp 228–231° dec, undepressed on admixture with an authentic sample of **2**.

Treatment of 7 with Acid. Formation of 3-Bromo-2-bromomethyl-6-methyl-4-pyrone (8).—The tetrabromo compound **7** (250 mg, 0.45 mmol) was added to hot sulfuric acid (5 ml) and the reaction mixture was heated for 25 min on the steam bath. The mixture was cooled and poured onto crushed ice. A reddish brown precipitate was obtained which was extracted with chloroform. The extract was washed with saturated aqueous sodium bicarbonate and water and dried. Removal of the solvent gave a dark brown, viscous oil (160 mg) that afforded brown crystals on standing. This product was chromatographed on silica gel in benzene; elution with 25% ether in benzene gave **8** as a colorless oil (150 mg, 60%) that crystallized on standing. After four recrystallizations from cyclohexane, **8** had mp 107–107.5°.

Anal. Calcd for $C_7H_6Br_2O_2$: C, 29.79; H, 2.13; Br, 56.74. Found: C, 29.56; H, 2.45; Br, 56.55.

Treatment of 2 with Bromine. Formation of 9 and 11.—The hexabromo compound **2** (144 mg, 0.2 mmol) suspended in chloroform (5 ml) was treated with a solution of bromine (70 mg, 0.44 mmol) in chloroform (2 ml), and the mixture was stirred for 12 days, after which the solid had gone into solution, the color of which was light yellow. An aliquot was withdrawn and worked up; it was found by infrared spectral comparison to consist mainly of the starting material. The remainder of the light yellow solution was treated with a dilute solution of bromine in chloroform from time to time and was stirred for another 45 days. The solution was washed with aqueous 10% sodium sulfite and water and dried. Removal of the solvent gave a pale yellow solid (120 mg) that was found to be a mixture of **2**, **9**, and **11** (5:3:9) by nmr spectral comparison. The solid was chromatographed on silica gel in benzene and eluted with 2% ether in benzene. The earlier fractions when recrystallized from benzene gave **9** as micro crystals, mp 214–216°, identified by mixture melting point and infrared and nmr spectral comparison. The middle fractions on recrystallization from benzene–petroleum ether gave **2**, mp 225–228°, identified by infrared spectral comparison.

Treatment of 9 with Acid. Formation of 3,5-Dibromo-2-dibromomethyl-6-methyl-4-pyrone (10).—The octabromo compound **9** (115 mg, 0.15 mmol) was suspended in concentrated sulfuric acid (5 ml), and the mixture was heated on a steam bath for *ca.* 12 hr, after which period the solid had dissolved, and the solution was dark brown. This mixture was cooled and poured onto crushed ice, when **10** precipitated as a white solid (101 mg, 88%). The crude material was purified by chromatography on silica gel in benzene and eluted with 25% ether in benzene to give **10** as needles, mp 142–145°. After three recrystallizations from cyclohexane, **10** had mp 144.5–146°.

Anal. Calcd for $C_7H_4Br_4O_2$: C, 19.09; H, 0.91; Br, 72.73. Found: C, 19.28; H, 0.94; Br, 72.70.

Treatment of 11 with Bromine. Formation of 9.—A solution of bromine (320 mg, 2.0 mmol) in chloroform (4 ml) was added dropwise to a stirred solution of **11** (120 mg, 0.15 mmol) in chloroform (2 ml) over a period of 4 days. The mixture was stirred for a further 3 days and then washed with aqueous 10% sodium sulfite and water. Removal of the solvent from the dried solution gave a pale yellow solid (121 mg), whose nmr spectrum indicated it to be a mixture of **9** and **11**. The mixture was chromatographed on silica gel in benzene and eluted with 2% ether in benzene. Early eluates gave a solid (67 mg) that was crystallized from benzene–petroleum ether to give **9** as micro crystals, mp 214–216°, identified by mixture melting point with an authentic sample, and infrared and nmr spectral comparison. Later eluates gave a solid (50 mg) that was shown to be the starting material **11** by infrared and nmr spectral comparison.

Treatment of 11 with Acid. Formation of 6 and 10.—The heptabromo compound **11** (210 mg, 0.262 mmol) when treated with concentrated sulfuric as described for **9** gave a mixture of **6** and **10** (175 mg). The mixture was chromatographed on silica gel in benzene. Elution with 5% ether in benzene gave a solid, which when recrystallized from cyclohexane gave **10**, mp 144–146°, identified by mixture melting point with an authentic sample, and infrared and nmr spectral comparison. Later eluates with 20% ether in benzene furnished a solid, which when recrystallized from cyclohexane gave **6**, mp 112.5–114°, identified by mixture melting point with an authentic sample, and infrared and nmr spectral comparison.

Irradiation of 2 and 9.—The solid hexabromo compound **2** was irradiated with a 450-W Hanovia medium-pressure mercury arc lamp; after 5 days the infrared and nmr spectra of the solid were identical with those of the starting material.

Similar irradiation of solutions of **2** or **9** in benzene for 3 hr gave brown, pungent-smelling products. Evaporation of the solvent gave a dark brown, thick oil that could not be purified by chromatography on silica gel.

Irradiation of the Bromopyrones 6 and 10.—Irradiation as above of the bromopyrones **6** and **10** in the solid state left them unchanged. When a solution of **10** (12 mg) in cyclohexane (1 ml) was irradiated in a quartz tube for 24 hr, it assumed a dark brown color. Removal of the solvent gave a pungent-smelling, dark brown viscous oil that was only partially soluble in chloroform.

Registry No.—**1**, 19034-31-2; **2**, 21543-87-3; **3**, 21543-88-4; **4**, 19083-62-6; **5**, 21558-26-9; **6**, 21558-22-5; **7**, 21543-89-5; **8**, 21558-23-6; **9**, 21543-90-8; **10**, 21558-24-7; **11**, 21543-91-9; 2,6-dimethyl-4-pyrone, 1004-36-0; bromine, 7726-95-6.

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