methylene chloride and 0.83 g (10 mmol) of **6a** was kept at room temperature to produce **39** in 8% yield.

Registry No.—**6a**, 7188-38-7; **7a**, 630-18-2; **7b**, 21864-76-6; **8a**, 21864-77-7; **8b**, 21864-78-8; **9a**, 21864-79-9; **12a**, 21864-80-2; **12b**, 21864-81-3; **15**, 21864-82-4; **16**, 21864-83-5; **18d**, 21864-84-6; **18e**, 21864-85-7; **30**, 21864-86-8; **33**, 21864-87-9; **36**, 21864-88-0; **38**, 21864-89-1; **39**, 21864-90-4; **43**, 21876-36-8; boron trifluoride diethyl ether, 109-63-7.

Photodimeric Cage Compounds. II. The Structure of the Photodimer of 2,6-Diethyl-4-pyrone[1]

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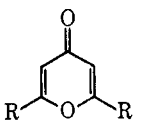
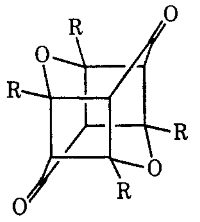
Spectroscopic and degradative studies show that the photodimer of 2,6-diethyl-4-pyrone has the head-to-tail cage structure **4**, analogous to that of the photodimer of 2,6-dimethyl-4-pyrone.

The photodimer[3] of 2,6-dimethyl-4-pyrone (**1**) has been shown to have the cage structure **2**.[1] This photodimerization is unusual in that it proceeds with regiospecificity[4] and stereospecificity to give a single *cis-syn-cis* head-to-tail dimer.[5] Irradiation of 2,6-diethyl-4-pyrone (**3**) also leads to a single photodimer, which has been assigned the cage structure **4** on the basis of the similarity of its properties to those of the dimer **2**.[6] We now report on an investigation of the chemistry of the photodimer of **3**, which fully establishes its structure as **4**.



1, R = CH_3
3, R = C_2H_5



2, R = CH_3
4, R = C_2H_5

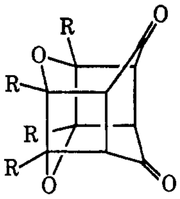
The monomer **3** was prepared from acetonedicarboxylic acid *via* treatment with propionic anhydride in the presence of sulfuric acid in an adaptation of the procedure of Deshapande.[7] Irradiation of **3** as the neat liquid, or better in solution in ethanol or benzene, led to the deposition of a solid dimer. In the latter solvent a 46% conversion to crystalline dimer, mp 273–275° dec, was realized after irradiation with a 450-W Hanovia medium-pressure arc lamp for 10 days; since the reaction solution contained *ca.* 50% of unconsumed monomer, the yield was *ca.* 90%. Comparison of the spectra of this dimer with those of the dimer of 2,6-dimethyl-4-pyrone (Table I) revealed a close similarity. The nmr spectrum of **2**, which has not been reported previously, and that of **4** are clearly in accord with the structural assignments. The unusually low-field position of the methine proton signals may be interpreted as due to deshielding by the neighboring carbonyl groups, in whose planes these protons are rigidly held. It must be emphasized, however, that these nmr spectra do not in themselves distinguish between the head-to-tail cage structures **2** and **4** and the corresponding head-to-head cage structures **5** and **6**, respectively.

Table I

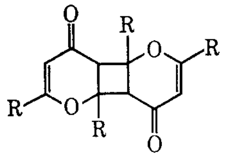
Spectra of the Photodimers of 2,6-Dimethyl- and 2,6-Diethyl-4-pyrone

Spectrum	2,6-Dimethyl-4-pyrone photodimer (**2**)	2,6-Diethyl-4-pyrone photodimer (**4**)
Infrared, $\lambda_{max}^{CHCl_3}$, μ	5.88, 6.90, 7.24	5.80,[a] 5.89, 6.90, 7.24
Ultraviolet, λ_{max}^{EtOH}, mμ	233 (ε 6600)[b]	236 (ε 6700)
Nuclear magnetic resonance, δ^{CDCl_3}, ppm	1.50 (s, 12 H) 3.18 (s, 4 H)	0.90 (t, *J* 7 Hz, 12 H) 1.72 (q, *J* 7 Hz, 8 H) 3.16 (s, 4 H)

[a] Shoulder. [b] Molecular extinction coefficient recorded for solution in acetonitrile; position of maximum unchanged.



5, R = CH_3
6, R = C_2H_5



7, R = C_2H_5
8, R = CH_3

The retention of the skeletal integrity of each of the monomer units in the dimer of **3** was established as in the case of the dimer of **1**[1] by the observation that treatment with aqueous methanolic hydrogen chloride returned the monomer in *ca.* 70% yield. Under milder acidic conditions it was possible to halt the reaction after the cleavage of a single cyclobutane ring and to isolate the *seco*-dimer **7**; this product was also obtained when the cage dimer was treated with ethyl-

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[1] Paper I: P. Yates and M. J. Jorgenson, *J. Amer. Chem. Soc.*, **85**, 2956 (1963).

[2] (a) Lash Miller Chemical Laboratories, University of Toronto, Toronto 5, Ontario, Canada; Alfred P. Sloan Foundation Fellow, 1957–1960; Hoffmann La Roche Fellow, 1961–1963; (b) Eastman Kodak Co. Fellow, Harvard University, 1959–1960; (c) Commonwealth Scholar, University of Toronto, 1963–1966.

[3] E. Paternò, *Gazz. Chim. Ital.*, **44**, I, 151 (1914); M. Giua and M. Civera, *ibid.*, **81**, 875 (1951).

[4] A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).

[5] *Cf.*, for example, P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2344 (1962); H. Ziffer, N. E. Sharpless, and R. O. Kan, *Tetrahedron*, **22**, 3011 (1966); P. Yates, S. N. Eğe, G. Büchi, and D. Knutsen, *Can. J. Chem.*, **45**, 2927 (1967); S. N. Eğe and P. Yates, *ibid.*, **45**, 2933 (1967); E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 3482 (1967); O. L. Chapman, P. J. Nelson, R. W. King, D. J. Trecker, and A. A. Griswold, *Rec. Chem. Progr.*, **28**, 167 (1967).

[6] P. Yates and E. S. Hand, *Tetrahedron Lett.*, 669 (1961); E. S. Hand, Ph.D. Thesis, Radcliffe College, 1961.

[7] S. S. Deshapande, *J. Indian Chem. Soc.*, **9**, 303 (1932).

magnesium bromide in tetrahydrofuran. In the latter case, steric factors presumably inhibit attack at the carbonyl carbon atoms and the Grignard reagent acts only as a Lewis acid. The analog of **7** in the methyl series, **8**, was first obtained by pyrolysis of the dimer **2**;[1,8] it has subsequently been found that this product can also be formed by treatment of **2** under mild acidic conditions.[9] The similarity of the spectra of **7** and **8** (Table II) is in accord with the assignment to them of analogous structures. As in the case of **8**, irradiation of **7** readily reconverts it to the cage dimer.

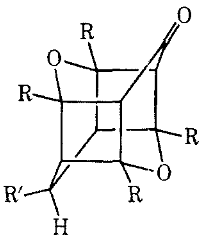
TABLE II

SPECTRA OF *seco*-DIMERS OF 2,6-DIMETHYL- AND 2,6-DIETHYL-4-PYRONE

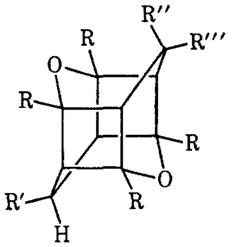
Spectrum	Compound **8**	**7**
Infrared, $\lambda_{max}^{CHCl_3}$, μ	6.04 (br),[a] 6.18	6.04 (br), 6.21
Ultraviolet, λ_{max}^{EtOH}, mμ	266 (ϵ 21,900)	265 (ϵ 22,700)
Nuclear magnetic resonance, δ^{CDCl_3}, ppm	1.70 (s, 6 H)	0.94 (t, *J* 7 Hz, 6 H)
	1.93 (s, 6 H)	1.06 (t, *J* 7 Hz, 6 H)
	3.10 (s, 2 H)	1.8–2.1 (*m*, 4 H)
	5.25 (s, 2 H)	2.20 (q, *J* 7 Hz, 4 H)
		2.95 (s, 2 H)
		5.05 (s, 2 H)

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

Although the dimer **2** was found to be readily susceptible to acid-catalyzed cleavage, it failed to undergo reaction in boiling aqueous sodium hydroxide.[1] This resistance to base-catalyzed cleavage is matched in the case of **4** by the fact that treatment with boiling ethanolic sodium ethoxide led only to reduction[10] of the carbonyl groups and not to cleavage. The major product obtained was a dihydro compound, shown by its infrared spectrum to be a hydroxy ketone ($\lambda_{max}^{CHCl_3}$ 2.78 and 5.91 μ); on acetylation it gave the corresponding keto acetate ($\lambda_{max}^{CHCl_3}$ 5.76 5.91 μ) from which it could be regenerated by hydrolysis. On oxidation with chromium trioxide it was reconverted to **4** and could thus be assigned the structure **9**. The ultraviolet spectra of **9** [λ_{max}^{EtOH} 225 mμ (ϵ 3000)] and its acetate (**10**) [λ_{max}^{EtOH} 225 mμ (ϵ 3500)] resemble closely the spectrum of the ketone **11** [λ_{max}^{EtOH} 223 mμ (ϵ 3500)].[1] Wolff–Kishner reduction of **9** gave **12**, the analog of one of the products formed on catalytic hydrogenation of the dimer **2**.[1] A second product obtained from the reaction of **4** with ethanolic sodium ethoxide was found to be a tetrahydro compound; it showed hydroxyl, but no carbonyl, absorption in its infrared spectrum and is considered to be the diol **13a** formed by reduction of both of the carbonyl groups of **4**. It was shown to be identical with one of two isomeric products formed on reduction of **4** with lithium aluminum hydride. It is assigned the diol structure of lower symmetry, **13a**, because it is the lower melting isomer. The other isomer is assigned the centrosymmetric structure **13b**; it is probably formed also in the reaction of **4** with ethanolic sodium ethoxide (see Experimental Section).



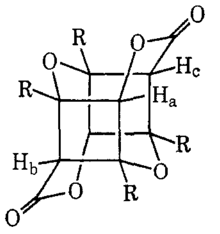
9, R = C_2H_5; R' = OH
10, R = C_2H_5; R' = $OCOCH_3$
11, R = CH_3; R' = H



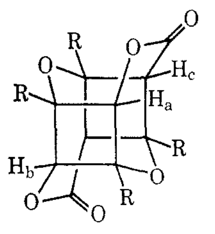
12, R = C_2H_5; R' = OH, R''; R''' = H
13a, R = C_2H_5; R', R'' = OH; R''' = H
13b, R = C_2H_5; R', R''' = OH; R'' = H
14, R = C_2H_5; R', R'', R''' = H
15, R = CH_3; R', R'', R''' = H

Wolff–Kishner reduction of **4** gave a product, $C_{18}H_{28}O_2$, lacking both hydroxyl and carbonyl absorption in its infrared spectrum, which is assigned structure **14**. Both this product and the analogous compound **15** prepared from **2**[1] show in their nmr spectra ($CDCl_3$) signals assignable to the C(sp^3)–CH_2CH_3 and C(sp^3)–CH_3 protons, respectively, together with an eight-proton singlet at δ *ca.* 2.0 ppm. The unexpected simplicity of these spectra requires that there be an accidental degeneracy of the signals due to the cyclobutyl protons and the annular methylene protons of **14** and **15**. That such is the case was demonstrated by recording the spectrum of **15** in benzene solution, when the singlet at δ 2.06 ppm was replaced by a symmetrical multiplet centered at 1.82 ppm as anticipated for the A_2B_2 systems, $CHCH_2CH$, present in **15**. The spectrum ($CDCl_3$) of the mono ketone **11** is in accord with expectation, showing a broadened twelve-proton singlet at δ 1.37 (two pairs of CH_3 protons in slightly different environments), two two-proton triplets at 1.89 and 2.40 ppm (*J* 2 Hz; A_2X_2 system, $CHCH_2CH$), and a two-proton singlet at δ 2.96 ppm (methine protons adjacent to the carbonyl group). It may be noted that the upfield shift of the cyclobutyl proton signal of **15** and of one of the cyclobutyl proton signals of **11** relative to the cyclobutyl signals of **2** and **4** is in accord with the earlier suggestion that the unusually low-field position of these signals in the spectra of **2** and **4** is due to deshielding by the carbonyl groups.

All of the data cited thus far confirm the assignment of a cage structure of type **4** to the photodimer of **3**, but do not distinguish between structure **4** and the corresponding head-to-head structure **6**. That this dimer does in fact have the head-to-tail structure **4** was shown by Baeyer–Villiger oxidation with excess *m*-chloroperbenzoic acid in benzene. This gave the two dilactones **16**, mp >350°, and **17**, mp 299–300°, in 57 and 30% yield, respectively.[11] Comparison of their



16, R = C_2H_5
18, R = CH_3



17, R = C_2H_5
19, R = CH_3

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[8] P. Yates and D. J. MacGregor, *Chem. Commun.*, 1209 (1967).

[9] D. J. MacGregor, Ph.D. Thesis, University of Toronto, 1967.

[10] *Cf.* R. B. Woodward and P. Yates, *J. Amer. Chem. Soc.*, **85**, 553 (1963).

[11] It was observed that when the oxidation of **4** was carried out with *m*-chloroperbenzoic acid in a 1:1 mixture of chloroform and dichloromethane, products similar to these were obtained; however, they were contaminated with chlorine-containing products from which they could not be separated by crystallization from a variety of solvents.

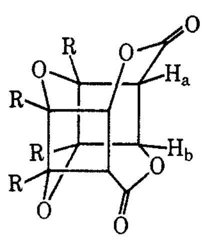
TABLE III

SPECTRA OF DILACTONES FORMED ON BAEYER–VILLIGER OXIDATION OF 2,6-DIMETHYL- AND 2,6-DIMETHYL-4-PYRONE

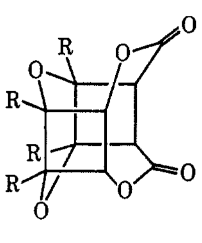
	Dilactones from **4**		Dilactones from **2**	
Spectrum	**16** (mp >350°)	**17** (mp 299–300°)	**18** (mp 340–350°)	**19** (mp *ca.* 280°)
Infrared, $\lambda_{max}^{CDCl_3}$, μ	5.76	5.76	5.75	5.75
Ultraviolet,[a] $\epsilon_{220}^{CH_3CN}$	440	620	480	930
Nuclear magnetic resonance, δ^{CHCl_3}, ppm	1.02 (t, *J* 7 Hz, 12 H) 1.82 (q, *J* 7 Hz, 8 H) 3.32 (d, *J* 1.5 Hz, 2 H) 4.27 (d, *J* 1.5 Hz, 2 H)	1.02 (t, *J* 7 Hz, 6 H)[b] 1.03 (t, *J* 7 Hz, 6 H)[b] 1.82 (q, *J* 7 Hz, 8 H) 3.45 (s, 2 H) 4.17 (s, 2 H)	1.65 (s, 12 H)[c] 3.63 (d, *J* 1.5 Hz, 2 H)[c] 4.53 (d, *J* 1.5 Hz, 2 H)[c]	1.59 (s, 6 H)[b] 1.61 (s, 6 H)[b] 3.57 (s, 2 H) 4.22 (s, 2 H)

[a] End absorption only. [b] Combined area of two close-lying signals corresponds to a total of 12 H. [c] In trifluoroacetic acid.

infrared and ultraviolet spectra with those of the corresponding dilactones (**18** and **19**, respectively) from **2** (Table III) established their gross structure. Their nmr spectra confirmed the assignment of the more highly symmetrical structure, **16**, to the higher melting, less soluble isomer in that the spectrum of this dilactone showed a single triplet signal attributable to the methyl protons of the four equivalent ethyl groups; the spectrum of the other dilactone showed two triplet signals as expected for the methyl protons of the two pairs of equivalent ethyl groups in structure **17** (*cf.* the single methyl proton signal for **18** and the pair of methyl proton signals for **19**). The nmr spectra also permit the exclusion of the head-to-head structures **20** and **21** for the dilactones. For, were **20** the structure of one of them, the signals due to the vicinal cyclobutyl protons of type H$_a$ and H$_b$ (see **20**) should show a splitting appreciably greater than that observed (1.5 Hz).[12,13] The exclusion of the head-to-head dilactone structures in turn excludes the head-to-head structure **6** for the photodimer itself (similar arguments based on the nmr spectra of the dilactones from **2** lead to the exclusion of the head-to-head structures **22** and **23**, corroborating the earlier assignment on other grounds of the head-to-tail structures **18** and **19** to them and of the head-to-tail structure **2** to the photodimer). The splitting (*J* 1.5 Hz) of the cyclobutyl proton signals in the spectrum of **16** can be interpreted in terms of long-range coupling between protons of type H$_a$ and H$_b$ (see **16**).[12] This interpretation accounts for the fact that no splitting is observed for the cyclobutyl proton signals in the spectrum of **17**, since the protons of type H$_a$ and H$_b$ are then equivalent. Had the splitting of the signals in the case of **16** been due to long-range coupling between protons of type H$_a$ and H$_c$, it would be likely that the splitting would be preserved in the spectrum of **17**. Analogous considerations apply in the cases of **18** and **19**.

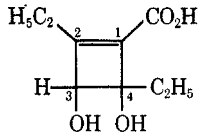


20, R = C$_2$H$_5$
22, R = CH$_3$

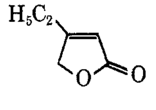


21, R = C$_2$H$_5$
23, R = CH$_3$

The structural assignment for the dilactone **16** was confirmed by degradation. Basic hydrolysis of **16** followed by acidification gave two crystalline products. A water-soluble compound, $C_9H_{14}O_4$, obtained in 34% yield can be assigned structure **24** on the basis of its spectral properties (see Experimental Section) and analogy with the hydrolysis of the dilactone **18**.[1]



24



25

The second product, $C_6H_8O_2$, was obtained in 32% yield and has been shown to have structure **25**. Its infrared spectrum in chloroform showed bands at 5.61, 5.71, 6.09 (w), and 11.23 (w) μ, with the band at 5.71 stronger than that at 5.61 μ; in carbon tetrachloride the corresponding bands appeared at 5.60, 5.70, 6.08 (w), and 11.35 (w) μ with the band at 5.60 much stronger than that at 5.70 μ. Such solvent-dependent doublets in the 5.6–5.7-μ region are characteristic of 2-butenolides with no α substituent,[14] and probably result from Fermi resonance between the carbonyl-stretching vibration and a close-lying overtone of the out-of-plane deformation of the α-C–H bond.[14,15] The ultraviolet spectrum (EtOH) of the compound $C_6H_8O_2$ showed an apparent maximum at 209 mμ (ϵ 11,700), also characteristic of 2-butenolides in which the ethylenic double bond is not fully substituted.[16] Its nmr spectrum showed a triplet at δ 1.22 (*J* 7.5 Hz, 3 H) and a quartet at δ 2.45 (*J* 7.5 Hz, 2 H) assigned to the vinylic ethyl protons in **25**, a multiplet at δ 4.76 ppm (2 H) assigned to the annular methylene protons, and a multiplet at δ 5.72 (1 H) assigned to the vinylic proton; the multiplicity of the latter signals is considered to be due to long-range coupling. The structural assignment was confirmed by the independent synthesis of **25** by a route devised earlier by Rubin, Paist, and Elderfield for the preparation of analogous 2-butenolides (Scheme I).[17]

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[12] I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967).

[13] Neither of the head-to-head dilactones **20** and **21** possesses four equivalent ethyl groups; however, it could be argued that in one case accidental degeneracy gives rise to a single methyl proton signal (*cf.* the accidental degeneracy of the methylene proton signals of **17**).

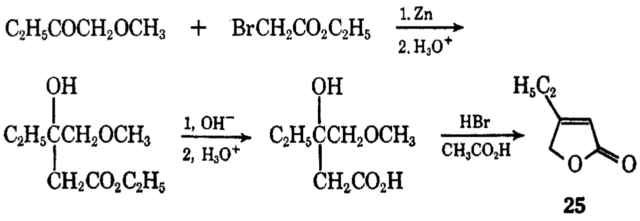
[14] R. N. Jones, C. L. Angell, T. Ito, and R. J. D. Smith, *Can. J. Chem.*, **37**, 2007 (1959).

[15] *Cf.* P. Yates and L. L. Williams, *J. Amer. Chem. Soc.*, **80**, 5896 (1958).

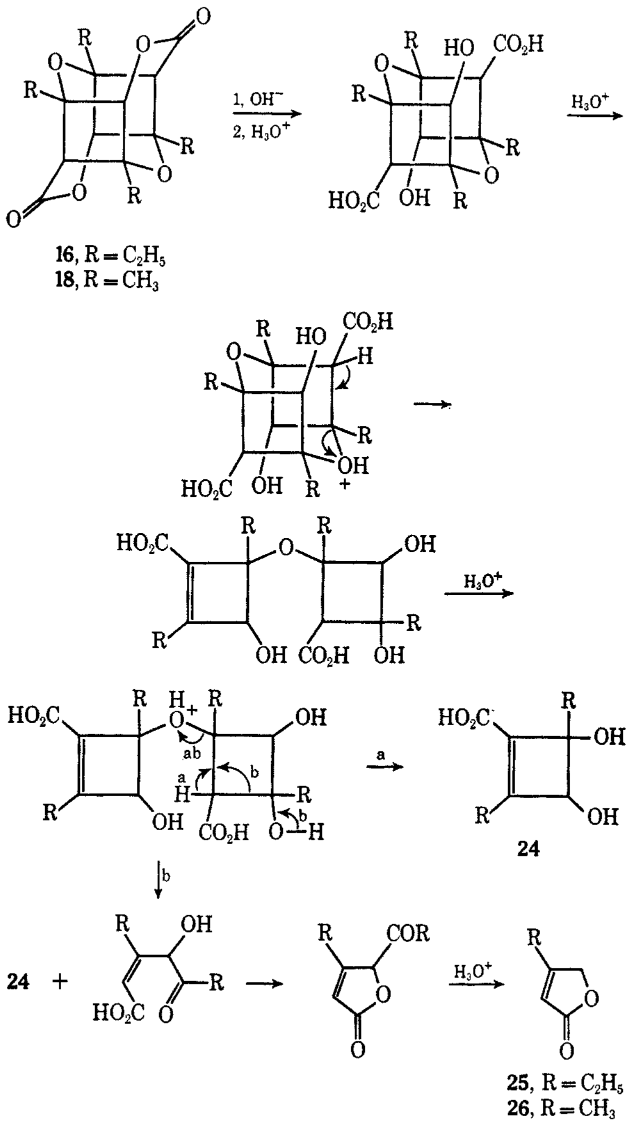
[16] *Cf.* J. Fried, R. G. Linville, and R. C. Elderfield, *J. Org. Chem.*, **7**, 362 (1942); G. R. Clemo and W. Cocker, *J. Chem. Soc.*, 30 (1946); L. H. Haynes and E. R. H. Jones, *ibid.*, 954 (1946); J. M. Ferland, Y. Lefebvre, R. Deghenghi, and K. Wiesner, *Tetrahedron Lett.*, 3617 (1966).

[17] M. Rubin, W. D. Paist, and R. C. Elderfield, *J. Org. Chem.*, **6**, 260 (1941).

SCHEME I

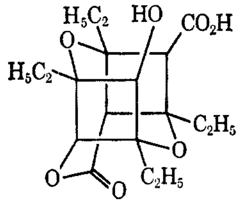


SCHEME II



Treatment of the unsaturated acid **24** with aqueous base followed by acidification led to recovery of 65% of the acid and an oil whose infrared spectrum showed no band at 5.60 μ and whose nmr spectrum showed no signal in the vinyl proton region. Thus **24** does not appear to be an intermediate in the formation of **25**. A reaction scheme which accounts for the formation of these two products from the dilactone **16** is shown in Scheme II.[18] Although it is possible to envisage variations in the details of this pathway, the formation of **25** requires that the dilactone have the head-to-tail structure **16** previously assigned. For although an analogous type of pathway can be envisaged for the hydrolytic cleavage of the head-to-head dilactone **20**, this would give a butenolide different from **25**. The same considerations also apply to the formation of the unsaturated acid **24**.[20]

Hydrolysis of the unsymmetrical dilactone **17** gave a complex mixture of products from which two crystalline products were isolated in low yield. One of these, $C_{18}H_{26}O_7$, is considered to have structure **27** and to arise by simple hydrolysis of one of the lactone rings of **17**. The other, $C_{18}H_{28}O_8$, is shown by its spectra to be related to the product, $C_{14}H_{20}O_8$, previously obtained in the hydrolysis of **19**, the unsymmetrical dilactone from **2**.[21]



27

Experimental Section

Melting points and boiling points are uncorrected. Unless specified otherwise, solutions in organic solvents were dried over anhydrous magnesium sulfate.

2,6-Diethyl-4-pyrone (3).[22]—Acetonedicarboxylic acid[23] (60.0 g, 0.41 mol) was added rapidly to propionic anhydride (170 ml, *ca.* 1.3 mol) containing concentrated sulfuric acid (2 ml), and the reaction mixture was heated on a steam bath for 20 min with occasional swirling. The solution was cooled rapidly in an ice-salt mixture, when a white solid mass was obtained. This was added to cold water (500 ml), stirred, and filtered immediately. The solid was again added to cold water (400 ml), and the mixture was stirred to give a slurry, which was filtered. The product was air-dried giving colorless plates (61 g, 60%), mp 113-115° (lit.[7] mp 114-115°).[24]

The above product (210 g, 0.88 mol) was placed in a 3-l. beaker and treated with hot water (1 l.) and aqueous 10% sodium carbonate (excess, *ca.* 600 ml), and the resulting paste was stirred with a glass rod and heated on a steam bath for 30 min. Carbon dioxide was evolved and a light yellow solution was obtained, which was heated at 85-90° for a further 80 min. The solution was cooled and acidified with aqueous 30% acetic acid until no more carbon dioxide was evolved. The white precipitate was filtered, washed with water, and air-dried to give 6-ethyl-4(2)-hydroxy-3-propionyl-2(4)-pyrone (141.0 g, 80%), mp 69-73° (lit.[7] mp 72°).

The above pyrone (141.0 g, 0.72 mol) was added to concentrated hydrochloric acid (350 ml) in a 2-l. round-bottomed flask, and the mixture was heated under reflux for 4 hr. The solution was cooled in ice and neutralized by stirring with solid sodium carbonate. The neutral solution was extracted thoroughly with chloroform. The extract was dried and stripped of solvent to give 2,6-diethyl-4-pyrone (**3**) as a brown liquid (110.5 g, 91%).

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(18) This scheme suggested that the dilactone **18** from **2** might also give rise to a 2-butenolide. Reinvestigation of the hydrolysis of this dilactone has in fact given evidence of the formation of **26** in low yield.[19]

(19) P. Yates, M. J. Jorgenson, and P. Singh, *J. Amer. Chem. Soc.*, **91**, 4739 (1969).

(20) Although the structure of this acid has been assigned here solely on the basis of analogy with the hydrolysis of dilactone **18**, independent evidence for the structural assignment **24** has been obtained. This will be presented in connection with a discussion of the stereochemistry of this and related compounds.[19]

(21) The structure originally assigned[1] to the compound, $C_{14}H_{20}O_8$, has been found to be inadmissible on the basis of nmr spectral evidence. Its structure and that of the compound $C_{18}H_{28}O_8$, obtained in the present work, will be discussed elsewhere: P. Yates, D. N. Butler, and P. Singh, to be submitted for publication.

(22) This is a modified version of the procedure of Deshapande;[7] the addition of sulfuric acid was found to be essential.

(23) R. Adams, H. M. Chiles, and C. F. Rassweiler, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p 10.

(24) This compound, previously considered to be 5-carboxy-6-ethyl-4(2)-hydroxy-3-propionyl-2(4)-pyrone,[7] is more probably 4(2),6-dihydroxy-3,5-dipropionyl-2(4)-pyrone.

Distillation gave **3** as a pale yellow liquid[25] (76.0 g), bp 110–115° (2 mm) [lit.[7] bp 136–138° (8 mm)]; $\lambda_{max}^{CHCl_3}$ 6.02, 6.22 μ; λ_{max}^{EtOH} 248 mμ (ϵ 14,600); δ^{CDCl_3} 1.22 (t, *J* 7.5 Hz, 6), 2.55 (q, *J* 7.5 Hz, 4), 6.03 (s, 2).

Photodimer of 2,6-Diethyl-4-pyrone (4).—A solution of 2,6-diethyl-4-pyrone (**3**) (36.0 g, 0.11 mol) in benzene (200 ml) was irradiated under nitrogen with a 450-W Hanovia medium-pressure mercury arc lamp contained in a water-cooled quartz well immersed in the solution. The irradiation was stopped from time to time, and the solid was scraped from the cooling jacket. After 10 days the solution had acquired a dark brown color, and irradiation was stopped. The crude dimer (17.80 g) was filtered; concentration of the filtrate afforded a further 1.4 g of the dimer. Removal of benzene from the filtrate after removal of the second crop of dimer gave a brown liquid (18.0 g, 50%) that was shown by infrared and nmr spectral comparison to consist almost entirely of **3**. Recrystallization of the crude dimer from chloroform–petroleum ether furnished **4** as white, shining needles (16.5 g, 46%): mp 273–275° dec; $\lambda_{max}^{CHCl_3}$ 5.80 (sh), 5.89, 6.90, 7.24 μ; λ_{max}^{EtOH} 236 mμ (ϵ 6700); δ^{CDCl_3} 0.90 (t, *J* 7 Hz, 12), 1.72 (q, *J* 7 Hz, 8), 3.16 (s, 4).

Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 70.94; H, 7.94.

Irradiation of **3** in ethanol or as the neat liquid also gave the photodimer **4**.

Reaction of the Photodimer 4 with Acid. Formation of 3 and the *seco* Dimer 7. A.—A mixture of the photodimer **4** (4.00 g), 10% hydrochloric acid (25 ml), and methanol (30 ml) was boiled under reflux overnight. The orange solution was concentrated under reduced pressure, and the residue was taken up in water. Solid sodium carbonate was added to pH 7, and the solution was extracted thrice with chloroform. The extract was dried over anhydrous sodium sulfate and stripped of solvent. Evaporative distillation of the residue gave 2,6-diethyl-4-pyrone (**3**) (2.78 g, 70%) as a pale yellow liquid, identified by infrared and nmr spectral comparison.

B.—A mixture of the photodimer **4** (0.10 g), 10% hydrochloric acid (10 ml), and 95% ethanol (15 ml) was boiled under reflux for 1 hr. The resulting yellow solution was concentrated under reduced pressure. The solid product (0.085 g, 85%) that separated was crystallized from petroleum ether to give **7** as needles, mp 150–154°, shown by mixture melting point and infrared spectral comparison to be identical with the product from the action of ethylmagnesium bromide on **4**.

Reaction of the Photodimer 4 with Ethylmagnesium Bromide. Formation of 7.—A solution of ethyl bromide (0.16 ml) in anhydrous tetrahydrofuran (20 ml) was added with stirring to magnesium (0.048 g) in anhydrous tetrahydrofuran (25 ml). After consumption of all of the magnesium a solution of the photodimer **4** (0.30 g) in tetrahydrofuran (75 ml) was added rapidly and stirring was continued for 1 hr. The mixture was treated with 10% hydrochloric acid (2.5 ml), and the organic layer was separated, dried over anhydrous sodium sulfate, and stripped of solvent. The black semisolid residue was chromatographed on silica gel (Davison 100–200 mesh, 18 g) in benzene. Elution with 10% ether in benzene gave **7** (0.10 g, 33%); crystallization from petroleum ether gave colorless needles: mp 152–154°; $\lambda_{max}^{CHCl_3}$ 6.04 (br), 6.21 μ; λ_{max}^{EtOH} 265 mμ (ϵ 22,700); δ^{CCl_4} 0.94 (t, *J* 7 Hz, 6), 1.06 (t, *J* 7 Hz, 6), 1.8–2.1 (m, 4), 2.20 (q, *J* 7 Hz, 4), 2.95 (s, 2), 5.05 (s, 2) ppm.

Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.02; H, 7.95. Found: C, 70.87; H, 7.94.

The deep red crystalline **2,4-dinitrophenylhydrazone** had mp 205–207°.

Anal. Calcd for $C_{30}N_{32}N_8O_{10}$: C, 54.21; H, 4.85; N, 16.86. Found: C, 54.09; H, 4.89; N, 16.59.

Reaction of the Photodimer 4 with Base. Formation of 9 and 13a.—The photodimer **4** (3.00 g) was added to a solution of sodium ethoxide prepared by reaction of sodium (1.1 g) with absolute ethanol (100 ml), and the mixture was boiled under nitrogen for 18 hr. The solution, whose color had changed from yellow to red to black, was cooled, the black insoluble material (0.70 g) was filtered, and the filtrate was concentrated to *ca.* 30 ml and poured into water. A brown precipitate (2.3 g) that could not be purified by crystallization was obtained. It was slurried with ethanol, and the slurry was poured onto a column composed of a 1:1 mixture of Norit and Celite (50 g). Elution with ethanol gave **9** (1.50 g) as colorless crystals, mp 181–183° after three crystallizations from benzene and one sublimation [130° (0.3 mm)]; $\lambda_{max}^{CHCl_3}$ 2.78, 5.91 μ; λ_{max}^{EtOH} 225 mμ (ϵ 2800). This sample was contaminated with some **13b** (*vide infra*).

Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.43; H, 8.69.

Compound **9** was unaffected by treatment with aqueous 10% hydrochloric acid at room temperature for 4 days.

The residue from the mother liquors (0.40 g) was treated with Girard's T reagent (0.25 g) in ethanol containing acetic acid (2 drops).[26] Extraction with chloroform gave a material that still showed weak ketonic absorption in its infrared spectrum and the procedure was repeated. The product was recrystallized three times from benzene–petroleum ether and sublimed to give **13a**, mp 148–149° (softening at 142°); $\lambda_{max}^{CHCl_3}$ 2.78 μ.

Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 69.83; H, 9.16.

Acetylation of 9. Formation of 10.—Compound **9** (0.22 g), prepared as above, was warmed on the steam bath for 2 hr with pyridine (2 ml) and acetic anhydride (2 ml). The solvents were evaporated in a stream of air, and the yellow residue was taken up in benzene and treated with Norit. The product was crystallized twice from petroleum ether and twice from methanol by cooling in a Dry Ice–acetone bath in each case, to give colorless needles (10 mg), mp 130–150°, which had a single peak at 5.78 μ in the carbonyl region of the infrared spectrum. This product is considered to be the diacetate of the diol **13b**, present as an impurity in the sample of **9**.

The material obtained from the mother liquors (0.17 g) had mp 73–91° and showed two bands in the carbonyl region of its infrared spectrum at 5.76 and 5.91 μ. It was purified by chromatography on Woelm neutral alumina (Grade 3, 10 g) in petroleum ether. Elution with 10% benzene in petroleum ether gave a mixture of acetates; elution with 50% benzene in petroleum ether gave the keto acetate **10**, which was recrystallized once from pentane and twice from methanol by cooling in a Dry Ice–acetone bath in each case and then had mp 96–97°; $\lambda_{max}^{CHCl_3}$ 5.76, 5.91 μ; λ_{max}^{EtOH} 225 mμ (ϵ 3500)

Anal. Calcd for $C_{20}H_{28}O_5$: C, 68.94; H, 8.10. Found: C, 68.87; H, 8.33.

Hydrolysis of 10. Formation of 9.—The keto acetate **10** (0.065 g) was dissolved in methanol (3 ml), and aqueous 10% sodium hydroxide was added. The solution was heated on the steam bath for 10 min and then cooled. The colorless crystals that separated were recrystallized twice from benzene–petroleum ether to give **9**, mp 190–191°; $\lambda_{max}^{CHCl_3}$ 2.78, 5.91 μ; λ_{max}^{EtOH} 225 mμ (ϵ 3000).

Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.47; H, 8.65.

Oxidation of 9. Formation of 4.—Chromium trioxide (0.50 g, 5 mmol) and compound **9** (0.25 g, 0.82 mmol) were added to acetic acid (15 ml). The mixture was stirred for 15 hr and then poured into water (50 ml). The precipitate was filtered and crystallized twice from chloroform–petroleum ether to give the photodimer **4**, identified by mixture melting point and infrared spectral comparison.

Wolff-Kishner Reduction of 9. Formation of 12.—A mixture of the hydroxy ketone **9**, mp 190–191° (0.50 g), potassium hydroxide (1.00 g), hydrazine hydrate (85%, 0.80 ml), and triethylene glycol (10 ml) was heated at 150° for 9 hr. The reaction mixture was cooled and poured into water (50 ml). The mixture was extracted with chloroform, and the extract was dried and stripped of solvent. The residue was crystallized from petroleum ether to give unconsumed **9** (60 mg). The residue from the mother liquor was chromatographed on silica gel (16 g) in benzene. Elution with 20% ether in benzene gave a solid (0.11 g), mp 105–107°, that on recrystallization from methanol afforded **12**, mp 106–107°.

Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 73.92; H, 9.60.

Reduction of the Photodimer 4 with Lithium Aluminum Hydride. Formation of 13a and 13b.—A solution of the photodimer **4** (0.30 g) in anhydrous tetrahydrofuran (60 ml) was added slowly to a stirred slurry of lithium aluminum hydride (0.15 g) in tetrahydrofuran, and the mixture was boiled under reflux for 2.5 hr. It was then decomposed with wet ethyl acetate (10 ml) and filtered. The residue was washed with chloroform (100 ml),

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[25] This color could be removed by a second distillation.

[26] *Cf.* L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955, p 89.

and the combined filtrate and washings were stripped of solvent to give a gummy solid. This was chromatographed on silica gel (18 g) in benzene. Elution with 2% ether in benzene gave a colorless solid (0.13 g), which on crystallization from benzene–petroleum ether gave **13b**, mp 178–179°; $\lambda_{\max}$ 2.78 μ.

Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.33; H, 9.04.

The residue from the mother liquors was rechromatographed on silica gel (12 g) in benzene. Elution with 2% ether in benzene gave in the later fractions a colorless solid (60 mg) which on crystallization from petroleum ether afforded **13a** as needles, mp 148–149°, shown by mixture melting point and infrared spectral comparison to be identical with the tetrahydro compound obtained by treatment of **4** with ethanolic sodium ethoxide.

Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.14; H, 9.04.

Wolff–Kishner Reduction of 4. Formation of 14.—The photodimer **4** (3.0 g), potassium hydroxide (5.0 g), and hydrazine (95%, 3.5 ml) were heated under reflux with triethylene glycol (40 ml) at 150° overnight. The reaction mixture was cooled, poured into water, and extracted with chloroform. The extract was dried over anhydrous sodium sulfate and stripped of solvent. The residual liquid (2.5 g) solidified on standing and was purified by evaporative distillation [60–80° (12 mm)] to give **14** (1.9 g, 70%). A second such distillation afforded an analytical sample: mp 49–50°; $\delta^{\mathrm{CDCl_3}}$ 0.88 (t, *J* 7 Hz, 12), 1.50 (q, *J* 7 Hz, 8), 1.95 (s, 8).

Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 77.96; H, 10.19.

Baeyer–Villiger Oxidation of 4. Formation of Dilactones 16 and 17.—A solution of the dimer **4** (16.0 g, 0.053 mol) and *m*-chloroperbenzoic acid (80.0 g, 0.50 mol) in benzene (1.5 l.) was heated at 50–55°. After *ca.* 6 hr, the reaction mixture became turbid, and a solid started to separate. The mixture was heated for another 12 hr and then cooled. The solid was filtered, washed thoroughly with aqueous sodium sulfite, aqueous 10% sodium bicarbonate, and water, and dried in an oven (90°) to give dilactone **16** (8.0 g). The filtrate was washed with aqueous sodium sulfite, aqueous sodium carbonate, and water and dried. Removal of the solvent gave a light yellow solid (11.5 g), which was dissolved in chloroform. The resulting solution liberated iodine from acidified aqueous potassium iodide, indicating the presence of peracid. It was stirred for 2 hr with solid potassium iodide (20.0 g) and 10% hydrochloric acid (50 ml). The violet aqueous layer was separated, and the chloroform layer was washed with aqueous 20% sodium thiosulfate, saturated aqueous sodium bicarbonate, and water and dried. Upon concentration of the solution to 100 ml, dilactone **16** (2.0 g) crystallized. Further concentration and crystallization gave a mixture of dilactones **16** and **17**, followed by dilactone **17** (5.15 g, 30%), which when recrystallized from benzene–petroleum ether had mp 299–299.5°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.76, 7.31 (w), 7.44 (w), 7.60 (m) μ; $\epsilon_{220}^{\mathrm{CH_3CN}}$ 620; $\delta^{\mathrm{CHCl_3}}$ 1.02 and 1.03 (two ts, *J* 7 Hz, 12), 1.82 (q, *J* 7 Hz, 8), 3.45 (s, 2), 4.17 (s, 2).

Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.28; H, 7.14. Found: C, 64.52; H, 7.09.

The combined crops of **16** (10.0 g, 57%) when recrystallized from dimethylformamide gave colorless needles, which did not melt below 350°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.76, 7.13 (m), 7.62 (m) μ; $\epsilon_{220}^{\mathrm{CH_3CN}}$ 440; $\delta^{\mathrm{CDCl_3}}$ 1.02 (t, *J* 7 Hz, 12), 1.82 (q, *J* 7 Hz, 8), 3.32 (d, *J* 1.5 Hz, 2), 4.27 (d, *J* 1.5 Hz, 2).

Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.28; H, 7.14. Found: C, 63.99; H, 7.07.

The dilactones **16** and **17** were also obtained by treatment of **4** with perbenzoic acid in benzene; however, the rate of formation of the dilactones was slower than that when *m*-chloroperbenzoic acid was used. When the reaction with perbenzoic acid was stopped at the stage when the product mixture showed equal intensity bands at 5.76 and 5.90 μ in its infrared spectrum, it was found possible to isolate a third product in low yield by fractional crystallization from benzene. This is considered to be the keto lactone formed by Baeyer–Villiger oxidation of a single carbonyl group of **4**: mp 280–285° dec; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.76, 5.90 μ.

Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.57; H, 7.57. Found: C, 67.46; H, 7.60.

When the oxidation of **4** was carried out with either *m*-chloroperbenzoic acid in a mixture of chloroform and methylene chloride (5:6 v/v) or perbenzoic acid in chloroform, products were obtained that closely resembled lactones **16** and **17** in their melting points and infrared spectra; however, these products contained chlorine and tenaciously retained this during attempted purification.

Base-Catalyzed Hydrolysis of 16. Formation of 24 and 25.—Finely ground **16** (9.0 g, 0.027 mol) was stirred under nitrogen with aqueous 15% sodium hydroxide (225 ml) for 80 hr, when a light brown solution was obtained. The solution was cooled in ice and acidified with cold 10% hydrochloric acid. The unconsumed dilactone **16** (5.7 g) was filtered; the filtrate was saturated with ammonium sulfate and extracted thoroughly with ethyl acetate. The extract was dried and stripped of the solvent to give a brown, viscous oil (2.90 g). The oil was triturated with carbon tetrachloride and allowed to stand, when **24** was obtained as a white solid (1.23 g, 34%, based on unrecovered **16**). After recrystallization from chloroform it had mp 101–102°; $\lambda_{\max}^{\mathrm{KBr}}$ 2.99, 3.25–4.25 (complex), 5.91 (sh), 5.96, 6.10 μ; $\lambda_{\max}^{\mathrm{EtOH}}$ 214 mμ (ϵ 7,800); $\delta^{\mathrm{D_2O}}$ 0.92 and 1.13 (two t's, *J* 7.5 Hz, 6), 1.63–2.20 (m, 2), 2.22–2.82 (m, 2), 4.58 (s, 1), 4.82 (HOD); $\delta^{\mathrm{CDCl_3}}$ 0.92 and 1.13 (two t's, *J* 7.5 Hz), 1.5–2.0 (m), 2.3–2.8 (m), 4.42 (br s), 6.20 (br s).

Anal. Calcd for $C_9H_{14}O_4$: C, 58.06; H, 7.53. Found: C, 57.71; H, 7.48.

The carbon tetrachloride solution was washed with aqueous 5% sodium bicarbonate and water and dried. Removal of the solvent gave **25** as a light brown liquid (0.70 g, 32%, based on unrecovered **16**), which afforded a white solid, mp 29–31°, when distilled at 50° (0.03 mm). One sublimation at room temperature (0.03 mm) furnished colorless needles: mp 36–37°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.61 (m), 5.71, 6.09 (w), 11.23 (w) μ; $\lambda_{\max}^{\mathrm{CCl_4}}$ 5.60, 5.70, 6.08 (w), 11.35 (w) μ; $\lambda_{\max}^{\mathrm{EtOH}}$ 208.5 mμ (ϵ 11,700); $\lambda_{\max}^{\mathrm{CH_3CN}}$ 204 mμ (ϵ 15,000); $\delta^{\mathrm{CDCl_3}}$ 1.22 (t, *J* 7.5 Hz, 3), 2.45 (q, *J* 7.5 Hz, 2), 4.67 (m, 2), 5.72 (m, 1).

Anal. Calcd for $C_6H_8O_2$: C, 64.29; H, 7.14. Found: C, 64.36; H, 7.31.

This was shown to be 3-ethyl-2-butenolide (**25**) by mixture melting point and spectral comparison with an authentic sample (*vide infra*).

Ethyl 3-Hydroxy-3-(methoxymethyl)pentanoate.—Methoxymethyl ethyl ketone was prepared by the method of Henze and Rigler:[27] $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.40, 5.75 (sh), 5.80, 9.00 μ; δ^{neat} 0.97 (t, *J* 7.5 Hz, 3), 2.46 (q, *J* 7.5 Hz, 2), 3.33 (s, 3), 3.95 (s, 2).

Methoxymethyl ethyl ketone (7.0 g, 0.069 mol), granulated zinc (washed with 10% hydrochloric acid, water, and ethanol, and dried; 4.60 g), and dry benzene (50 ml) were placed in a 250-ml three-necked flask, fitted with an efficient reflux condenser protected with a calcium chloride tube and a dropping funnel containing ethyl bromoacetate (11.7 g, 0.069 mol) in benzene (20 ml). The contents of the flask were boiled, and the solution of ethyl bromoacetate was added dropwise (*ca.* 20 min). The reaction mixture was heated under reflux for 2.5 hr and then cooled. The cold solution was acidified strongly (pH 2) with ice-cold 20% sulfuric acid, and the benzene layer was separated. The aqueous layer was extracted with benzene. The combined benzene layer and extracts were washed with saturated aqueous sodium bicarbonate and water and dried. Removal of the solvent gave ethyl 3-hydroxy-3-(methoxymethyl)pentanoate as a brown liquid (10.3 g, 80%), which when distilled afforded a colorless liquid: bp 106° (16 mm); $\lambda_{\max}^{\mathrm{CCl_4}}$ 2.85 (m), 5.83, 9.00 μ; δ^{neat} 0.89 (t, *J* 7.5 Hz, 3), 1.25 and 1.51 (t, *J* 7 Hz, and q, *J* 7.5 Hz, 5), 2.42 (s, 2), 3.26 and 3.32 (ss, 6), 4.12 (q, *J* 7 Hz, 2); after being washed with D_2O, the sample gave a spectrum which was essentially unchanged in the position of the signals, but the combined 3.26 and 3.32 signals now corresponded to 5 H.

Anal. Calcd for $C_9H_{18}O_4$: C, 56.84; H, 9.47. Found: C, 56.86; H, 9.41.

3-Ethyl-2-butenolide (25).—A solution of the above ester (4.80 g, 0.025 mol) in ethanol (25 ml) and aqueous 5% sodium hydroxide (20 ml, 0.025 mol) was boiled under reflux for 4 hr. The solution was cooled and washed with chloroform. The alkaline aqueous solution was acidified with 10% hydrochloric acid. The acidic solution was extracted with chloroform; the chloroform extract was washed with water and dried. Removal of the solvent furnished 3-hydroxy-3-(methoxymethyl)-pentanoic acid as a colorless liquid (1.46 g, 36%): bp 110° (0.75 mm); $\lambda_{\max}^{\mathrm{CCl_4}}$ 2.83 (m), 3.00–4.02, 5.88, 9.00 μ; $\delta^{\mathrm{CCl_4}}$ 0.90 (t, *J* 7 Hz, 3), 1.57 (q, *J* 7 Hz, 2), 2.51 (s, 2), 3.35 (s, 5), 7.50 (br s, 2).

The hydroxy acid (1.00 g, 0.0062 mol) was added to glacial acetic acid (20 ml) presaturated with hydrogen bromide, and the

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[27] H. R. Henze and N. E. Rigler, *J. Amer. Chem. Soc.*, **56**, 1350 (1934).

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.

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

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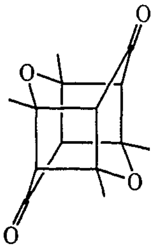
Reaction of the cage photodimer of 2,6-dimethyl-4-pyrone with liquid bromine gives tetrabromo, hexabromo, heptabromo, and octabromo substitution products of the *seco*-dimer **3**. Treatment of these products with sulfuric acid cleaves the remaining cyclobutane ring and gives dibromo, tribromo, and tetrabromo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

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