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The Photochemistry of 4,5-Disubstituted 1,3-Dioxolen-2-ones

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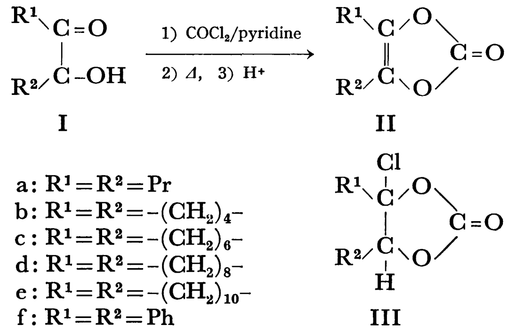
The benzene-sensitized photoreaction of 4,5-dipropyl- (IIa) and 4,5-tetramethylene-1,3-dioxolen-2-one (IIb) in isopropyl alcohol gives two reduction products, *cis*- (V) and *trans*-4,5-disubstituted 1,3-dioxolan-2-one (VI). The irradiation of octa- (IId) and decamethylene-bridged vinylene carbonate (IIe) results in transannular hydrogen atom transfer from a methylene group to the olefinic bond and a subsequent recombination affording three tricyclic products, IX, X, and XIX. An examination of the stereochemistry of the products has indicated the participation of a diradical intermediate.

1,3-Dioxolen-2-ones (vinylene carbonates) are useful synthetic intermediates.[1] Recent reports have dealt with their photochemical dimerization[2] as well as with their cycloaddition reaction to olefins[3] and acetylenes.[4] We first wanted to obtain a general method for the preparation of 4,5-disubstituted derivatives, and then we proceeded to examine the photochemical behavior[5] of the derivatives.

Preparation of 4,5-Disubstituted 1,3-Dioxolen-2-ones. The known route to vinylene carbonates consisted of the chlorination of ethylene carbonates and a subsequent dehydrochlorination.[6] Vinylene carbonates are carbonic acid esters of ene-diols which are tautomeric with acyloins.[7] The treatment of an acyloin (I) with phosgene in the presence of pyridine afforded monochlorinated ethylene carbonate, III. The direct distillation of III caused a thermal dehydrochlorination, thus giving a crude vinylene carbonate, II (Scheme 1).



I

II

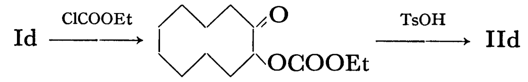
III

a: $R^1=R^2=Pr$
b: $R^1=R^2=-(CH_2)_4-$
c: $R^1=R^2=-(CH_2)_6-$
d: $R^1=R^2=-(CH_2)_8-$
e: $R^1=R^2=-(CH_2)_{10}-$
f: $R^1=R^2=Ph$

Scheme 1.

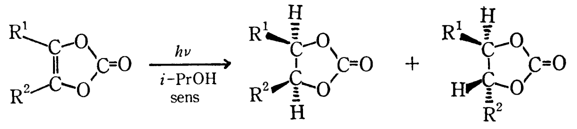
As the NMR spectrum showed contamination by exocyclic isomer(s), the crude carbonate, II, was converted to a pure form by heating a mixture dissolved in xylene with *p*-toluenesulfonic acid. The resulting II showed satisfactory NMR signals (no olefinic protons).

The carbonate, IId, was also prepared by the ethoxycarbonylation of sebacoin (Id) with ethyl chloroformate followed by treatment with *p*-toluenesulfonic acid in boiling xylene (Scheme 2).



Scheme 2.

Photoreduction. The UV irradiation of IIa in isopropyl alcohol containing a benzene sensitizer afforded *cis*-4,5-dipropyl-1,3-dioxolan-2-one (Va) and its *trans* isomer (VIa), along with two dimers of IIa and acetone pinacol. The ratio of Va/VIa was determined by gas chromatography (GC) to be 8 : 92, (Scheme 3). The structures of the products were established by comparison with authentic samples prepared by the esterification of *meso*- and *dl*-4,5-octanediol[8] with phosgene.



II V VI

a: $R^1=R^2=Pr$; b: $R^1=R^2=-(CH_2)_4-$

Scheme 3.

On the other hand, the UV irradiation of IIa in acetone gave only two kinds of dimers. The stereochemistry of the dimers was not examined.

The tetramethylene derivative, IIb, gave two saturated products, Vb and VIb (19% yield, 89: 11), upon irradiation in isopropyl alcohol–benzene. In the absence of hydrogen donors, IIb resisted the photoreaction.

The hexamethylene derivative, IIc, behaved differently and gave only a dimer upon irradiation both in acetone and in isopropyl alcohol–benzene.

Since the photoreaction of II required the presence

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1) a) M. S. Newman and R. W. Addor, *J. Amer. Chem. Soc.*, **77**, 3789 (1955). b) M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961). c) J. C. Hinshaw, *Chem. Commun.*, **1971**, 630. d) H.-D. Scharf and H. Seidler, *Angew. Chem.*, **82**, 935 (1970). e) H.-D. Scharf and R. Klar, *Ann. Chem.*, **739**, 166 (1970). f) H.-D. Scharf and R. Klar, *Tetrahedron Lett.*, **1971**, 517. g) G. Hesse and P. Lechtken, *Angew. Chem.*, **83**, 143 (1971).

2) W. Hartmann and R. Steinmetz, *Chem. Ber.*, **100**, 217 (1967).

3) W. Hartmann, *ibid.*, **101**, 1643 (1968).

4) a) R. H. Grubbs, *J. Amer. Chem. Soc.*, **92**, 6693 (1970). b) J. Tancrede and M. Rosenblum, *Synthesis*, **1971**, 219.

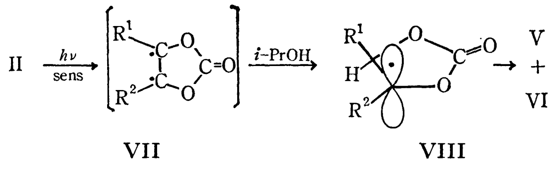
5) A part of this work has previously been communicated: T. Hiyama, S. Fujita, and H. Nozaki, This Bulletin, **44**, 3222 (1971).

6) a) M. S. Newman, R. W. Addor, *J. Amer. Chem. Soc.*, **75**, 1263 (1953). b) N. D. Field and J. R. Schaefgen, *J. Polym. Sci.*, **58**, 533 (1962). c) J. R. Schaefgen and N. D. Field, *Macromol. Syn.*, **2**, 15 (1966). d) L. R. Morris, U. S. 3125582 (1964); *Chem. Abstr.*, **60**, 13248g (1964).

7) Schering Akt-Ges., Ger. 1044104 (1958); *Chem. Abstr.*, **55**, 4533h (1961).

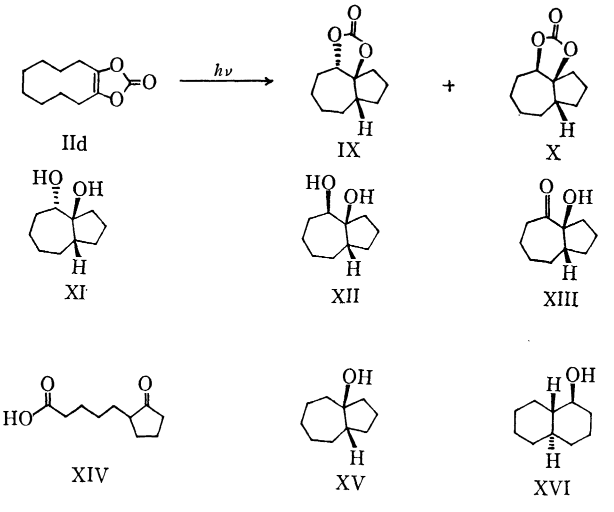
8) The compound was obtained by sodium borohydride reduction of butyroin, followed by chromatographic separation. See J. Wiemann, G. Dana, Sa-Le-Thi-Thuan, and M. Brami, *Compt. Rend.*, **258**, 3724 (1964).

of triplet sensitizers,[2] such as acetone and benzene, the reaction must involve the triplet state of the olefinic functional group as a diradical. The photochemical behavior of the ene-diol carbonate moiety of II may be understood in the same way as the photoreduction of cyclopentenes.[9] The triplet state, VII, abstracts a hydrogen atom from isopropyl alcohol to produce the VIII radical stabilized by the adjacent oxygen atom. This then yields a mixture of ethylene carbonate isomer (V and VI), in which the thermodynamically more stable one predominates (Scheme 4).



Scheme 4.

Intramolecular Hydrogen Abstraction. The irradiation of IId in acetone gave no dimers, but a mixture of novel tricyclic stereoisomers, IX and X, in a 71% yield. As the separation of the two isomers failed, the mixture was hydrolyzed to the *vicinal* diols, XI and XII (Scheme 5). The ratio of XI/XII was determined by GC as 85: 15. The separation of the two diols was accomplished by preparative thin-layer chromatography (plc).



Scheme 5.

The structure and stereochemistry of XI and XII were established as follows. Since the oxidation of XI and XII by *N*-bromosuccinimide (NBS)[12] gave the same ketol, XIII, the diols should have the same ring system and ring fusion. The absorption of XIII at 1700 cm^{-1} implied that the ring including the carbonyl group was medium-sized. The glycol cleavage of XI and XII with periodate-permanganate[13] afforded ε-(2-ketocyclopentyl)valeric acid (XIV).[14] Hence, both XI and XII were established to have a bicyclo[5.3.0]decane structure. The *cis*-ring fusion of the photoproducts was determined by the fact that the half-tosylation of a mixture of XI and XII, followed by reduction with lithium aluminum hydride or sodium borohydride, afforded *cis*-bicyclo[5.3.0]decane-1-ol (XV), along with *trans,trans*-α-decalol (XVI).[15] The formation of the latter can be ascribed to the base catalyzed rearrangement of the half-tosylate,[16] followed by the reduction of the resulting *trans*-α-decalone. In fact, the treatment of the half-tosylate of XI and XII with sodium methoxide in methanol afforded *trans*-α-decalone.

The reduction of XIII with sodium bis(2-methoxyethoxy)aluminum hydride (VSH) yielded XI almost exclusively. On the basis of Cram's rule,[17] the *trans*-configuration of the *vicinal* hydroxyl groups of XI was established, and consequently XII turned out to be its *cis*-diol isomer. Thus, XI and XII were concluded to be *cis*-bicyclo[5.3.0]decane-*trans*-1,2-diol and its *cis*-diol isomer respectively. The transannular photoreaction of IId proceeded even in isopropyl alcohol upon benzene sensitization, and neither reduction products nor dimers were detected among the products.

An inspection of the Dreiding models of IId suggests that the hydrogen atom on the C-6 in the excited state[18] resides closest to the C-1 (XVII) and that the abstraction of H_A by the C-1 radical probably occurs *via* seven-membered cyclic transition state. A subsequent recombination[19] of the resulting diradical, XVIII, may account for the preference for IX.

The decamethylene derivative, IIe, proved to be rather less reactive than IId. The irradiation of an

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[9] It has been well known that acyclic and large ring olefins undergo the *cis-trans* isomerization (Ref. 10) upon triplet sensitization, and that four- or five-membered cyclic olefins are reduced by hydrogen abstraction of the double bond (Ref. 11).

[10] A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry", John Wiley and Sons, Inc., New York (1969), pp. 143, 153.

[11] For four-membered ring, see a) R. L. Cargill, J. R. Damewood, M. M. Cooper, *J. Amer. Chem. Soc.*, **88**, 1330 (1966). For five-membered ring, see b) R. R. Sauers, W. Schinski, and M. M. Mason, *Tetrahedron Lett.*, **1967**, 4763. c) P. J. Kropp, *J. Amer. Chem. Soc.*, **89**, 3650 (1967). d) H.-D. Scharf, *Tetrahedron*, **23**, 3057 (1967). e) T. M. Gund, V. Z. Williams, Jr., E. Osawa. and P. von R. Schleyer, *Tetrahedron Lett.*, **1970**, 3877. f) L. Vollner, H. Parler, W. Klein, and F. Korte, *Tetrahedron*, **27**, 501 (1971).

[12] L. F. Fieser and S. Rajagopalan, *J. Amer. Chem. Soc.*, **71**, 3938 (1949).

[13] M. E. Wall and S. Serota, *J. Org. Chem.*, **24**, 741 (1959),

[14] W. Herz, *ibid.*, **22**, 630 (1957).

[15] W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Amer. Chem. Soc.*, **76**, 4420 (1954).

[16] Similar rearrangements have been reported previously. For example, see a) G. Büchi, W. Hofheinz, and J. V. Paukstelis, *J. Amer. Chem. Soc.*, **91**, 6473 (1969). b) C. A. Grob, H. R. Kiefer, H. Lutz, and H. Wilkens, *Tetrahedron Lett.*, **1964**, 290. c) E. J. Corey, R. B. Mitra, and H. Uda, *J. Amer. Chem. Soc.*, **85**, 362 (1963).

[17] D. J. Cram and K. R. Kopecky, *ibid.*, **81**, 2748 (1959).

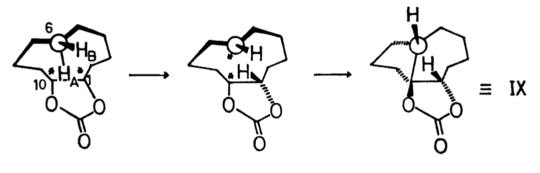
[18] A carbon-carbon double bond is well known to be twisted in its triplet state, see Ref. 10, p. 137.

[19] Recombination of a diradical is known to occur with retention of the configuration at the radical centers separated by intervening one methylene, whereas it proceeds with partial inversion if the radical centers are separated by three or more methylenes. See C. G. Overberger and J. Anselme, *J. Amer. Chem. Soc.*, **84**, 869 (1962). The absence of *trans*-fused bicyclo[5.3.0]decanes in the photoproducts suggest that the recombination of the diradical XVIII precedes any conformational change. The reason is not clear yet, but may be explained by assuming fast spin-inversion at the radical center (C-10) adjacent to a hetero atom.

TABLE 1. PHYSICAL PROPERTIES OF 1,3-DIOXOLEN-2-ONES. II

Compound	Yield (%)	Bp (°C)/mmHg |Mp| (Solvent)	IR[a] (cm^{-1})	NMR[b] (δ)
IIa[c]	69	90—93/4	1830 1200 1030	1.97 (t, 6H, CH_3–), 1.62 (sextet, 4H, CH_2), 2.37 (t, 4H, CH_2C=)
IIb[d]	34	120—125/21	1820 1750 1200 940	1.0—2.1 (m, 4H), 2.1—2.7 (m, 4H)
IIc[e]	56	94—106/2	1820 1730 1710 1130 1040	1.0—2.3 (m, 12H, methylenes), 2.55 (t, 4H, CH_2C=)
IId[f]	80 67[h]	|44—45| (*n*-hexane)	1830 1730 1184[g] 1170 1130 1010	0.9—1.9 (m, 12H, methylenes), 2.45 (t, 4H, CH_2C=)
IIe[i]	50	|53.5—54| (*n*-hexane)	1825 1728 1215[g] 1142	1.1—2.0 (m, 16H, methylenes), 2.35 (t, 4H, CH_2C=)

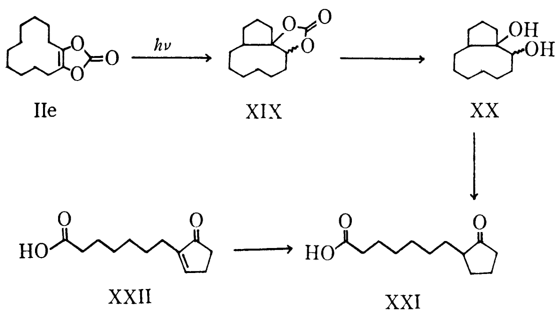
a) Neat unless otherwise stated. b) Determined in CCl_4 at 24°C, 60 MHz. c) Found: C, 63.3; H, 8.3%. Calcd for $C_9H_{14}O_3$: C, 63.5; H, 8.3%. MS: *m/e* (relative abundance) 170 (M^+, 18), 141 (43), 83 (47), 71 (33), 69 (34), 55 (100) 44 (70). d) Found: C, 60.2; H, 6.0%. Calcd for $C_7H_8O_3$: C, 60.0; H, 5.8%. MS: *m/e* (relative abundance) 140 (M^+, 54), 112 (13), 95 (14), 68 (100), 67 (80), 55 (98). e) Found: C, 64.4; H, 7.2%. Calcd for $C_9H_{12}O_3$: C, 64.3; H, 7.2%. MS: *m/e* (relative abundance) 168 (M^+, 29), 95 (26), 81 (48), 68 (61), 67 (88), 55 (100). f) Found: C, 67.6; H, 8.2%. Calcd for $C_{11}H_{16}O_3$: C, 67.3; H, 8.2%. MS: *m/e* (relative abundance) 196 (M^+, 34), 137 (3), 123 (10), 109 (20), 97 (34), 95 (40), 81 (60), 67 (78), 55 (100), 41 (88). g) Nujol mull. h) Prepared by ethoxycarbonylation of sebacoin, followed by acid-treatment, *vide infra*. i) Found: C, 69.4; H, 9.0%. Calcd for $C_{13}H_{20}O_3$: C, 69.6; H, 9.0%. MS: *m/e* (relative abundance) 224 (M^+, 20), 151 (2), 137 (6), 123 (8), 111 (14), 109 (14), 98 (44), 95 (30), 81 (40), 67 (48), 55 (100).



XVII XVIII

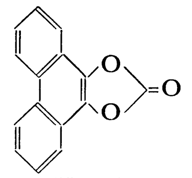
Scheme 6.

acetone solution of IIe yielded XIX in a 49% yield, along with a recovery of IIe (21%) (Scheme 7). The presence of the stereoisomers was not excluded, as no satisfactory separation of the isomers was accomplished. Alkaline hydrolysis gave the *vicinal* diol, XX, which was then subjected to Rudloff oxidation to afford 7-(2-ketocyclopentyl)heptanoic acid (XXI). IR bands of the keto acid appeared at 1737, and 1708 cm^{-1}, characteristic of a five-membered ketone and a carboxylic acid respectively. An authentic sample of XXI was obtained by the hydrogenation of the unsaturated derivative (XXII).[20] Consequently, the structure of XIX was established to be bicyclo[7.3.0]-dodecane-1,2-diol. The stereochemistry of the *vicinal* hydroxyl groups and the mode of the ring fusion were not examined.



Scheme 7.

The diphenylvinylene carbonate, IIf, was recovered unchanged upon irradiation in cyclohexane, whereas the photoreaction of IIf in the presence of iodine gave a phenanthrene derivative, XXIII, in a 77% yield.



XXIII

Experimental

All the temperatures are uncorrected. The infrared spectra were recorded on a Shimadzu spectrophotometer IR-27-G; the ultraviolet spectra, on a Hitachi EPS-2 spectrometer; the nuclear magnetic resonance spectra, on a JEOL-60-H spectrometer, and the mass spectra, on a Hitachi RMU-6L spectrometer.

Preparation of I. *General Procedure*: To a solution of an acyloin (50 mmol) in benzene (60 m*l*) and pyridine (90 m*l*), a mixture of a 30% toluene solution (55 g) of phosgene (167 mmol) and benzene (80 m*l*) was added, drop by drop, at 0°C; the mixture was then stirred overnight. After dilution with *n*-hexane (300 m*l*), the precipitated pyridinium chloride was filtered off. The filtrate was washed twice with water (100 m*l*) and dried over anhydrous potassium carbonate. The evaporation of the solvent *in vacuo* and subsequent distillation gave a mixture of II and its isomer(s). The distillate was dissolved in a xylene mixture (*ca.* 80 m*l*), after which the solution was heated to reflux for 24 hr in the presence of *p*-toluenesulfonic acid (*ca.* 1 g). Neutralization with pyridine, filtration, and distillation gave II. The yields and physical properties are summarized in Table 1.

4,5-Diphenyl-1,3-dioxolen-2-one (*IIf*). This was prepared much as has been described above. Distillation at 140—150°C/0.15 mmHg gave IIf in a 61% yield; it then crystallized; mp 71—73°C (lit,[7] 74—76°C (*n*-hexane)). IR (KBr): 1820, 1695, 1208, 1068, 995, 727, 692 cm^{-1}. MS: *m/e* (relative abundance) 238 (M^+, 3), 165 (13), 152 (5), 105 (100), 77 (64).

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[20] J. F. Bagli, T. Bogri, R. Deghenghi, and K. Wiesner, *Tetrahedron Lett.*, **1966**, 465. We are heartily grateful to Dr. Bagli for his kindness of sending us the sample of XXII.

4,5-Octamethylen-1,3-dioxolen-2-one (IId). An Alternate Procedure. Ethyl chloroformate (6 m*l*, 63 mmol) was added, drop by drop, to a solution of sebacoin (5.10 g, 30 mmol) in pyridine (30 m*l*) at room temperature, after which stirring was continued for 1 hr. The mixture was then diluted with *n*-hexane (100 m*l*), and the precipitated pyridinium chloride was filtered off. The solvents were evaporated *in vacuo* to yield ethyl 2-ketocyclodecyl carbonate quantitatively. IR (neat): 1750, 1728, 1260, 1010 cm^{-1}.

The unsymmetrical carbonate was directly mixed with *p*-toluenesulfonic acid (0.59 g, 3.4 mmol) in xylene (150 m*l*), and the whole was heated to reflux. After one day *p*-toluenesulfonic acid (1.18 g, 6.8 mmol) was added; the heating was then continued for another day. The acid was then neutralized with pyridine, and the precipitated salts were filtered off. Evaporation and distillation gave IId (3.97 g, 67%); bp 123—126°C/3 mmHg. The oil solidified and was recrystallized from *n*-hexane (see Table 1).

UV Irradiation of IIa in Acetone. A solution of IIa (1.14 g, 67 mmol) in acetone (50 m*l*) was placed in a quartz tube and irradiated with a 200-W high-pressure mercury lamp externally for 62 hr. The subsequent evaporation of the excess acetone *in vacuo* gave a crude solid (*ca.* 1.5 g), which was then recrystallized from *n*-hexane–ether–ethyl acetate to yield a dimer (0.05 g); mp 225—226°C. IR (Nujol): 1810, 1100, 1035 cm^{-1}. NMR (CDCl$_3$): δ 0.8—2.3 (m). MS: *m/e* (relative abundance) 171 (16), 170 (M$^+$/2, 100), 141 (30), 83 (18), 71 (25), 69 (8), 55 (22), 43 (66). Found: C, 63.6; H, 8.3%. Calcd for $C_{18}H_{28}O_6$: C, 63.5; H, 8.3%.

The mother liquid was subjected to chromatography on a silica gel column. Elution with benzene gave another crop of the crystalline dimer (0.18 g, totally, a 20% yield). Further elution gave an oily dimer (0.87 g, 76%); bp 100—110°C (bath temperature)/0.2 mmHg. IR (neat): 1810, 1212, 1131, 1032 cm^{-1}. NMR (CCl$_4$): δ 0.8—2.3 (m). MS: *m/e* (relative abundance) 170 (M$^+$/2, 28), 169 (11), 141 (21), 83 (20), 71 (59), 55 (43), 43 (100). Found: C, 63.5; H, 8.8%. Calcd for $C_{18}H_{28}O_6$: C, 63.5; H, 8.3%.

UV Irradiation of IIa in Isopropyl Alcohol-benzene. A mixture of IIa (1.12 g, 66 mmol), isopropyl alcohol (50 m*l*), and benzene (1 m*l*) was irradiated as has been described above for 5 days. Subsequent evaporation and distillation at 120—140°C/20 mmHg gave acetone pinacol (0.4 g). Further distillation (110°C/0.8 mmHg) gave a mixture of Va and VIa (0.22 g, 19%). The GC (High Vacuum Silicone Grease on Celite 545, 10%, 2 m) of the mixture revealed that the Va/VIa ratio was 8:92. Each component was separated by preparative GC (Silicone SE 30 on Chromosorb W, 30%, 1 m); the mass and infrared spectra and retention time on the GC were identical with those of the respective authentic samples (*vide infra*).

cis-*4,5-Dipropyl-1,3-dioxolan-2-one* (*Va*). Pyridine (2 ml) was added, drop by drop, at 0°C to a mixture of *meso*-4,5-octanediol (0.30 g, 2 mmol), benzene (10 m*l*), and a 30% phosgene solution in toluene (1.5 g). Stirring was continued overnight. A subsequent work-up gave Va quantitatively, bp 85—90°C (bath temperature)/3 mmHg. IR (neat): 1810, 1095, 1030 cm^{-1}. NMR (CCl$_4$): δ 0.8—2.1 (m, peak at δ 1.03 and 1.65, 14H, methyls and methylenes), 3.7—4.5 (m, 2H, CH–O). MS: *m/e* (relative abundance) 129 (M$^+$−43, 3), 128 (M$^+$−44, 1), 98 (4), 86 (9). 85 (11), 71 (16), 67 (26), 57 (68), 56 (61), 55 (53), 43 (84), 41 (100). Found: C, 62.9; H, 9.4%. Calcd for $C_9H_{16}O_3$: C, 62.8; H, 9.4%.

trans-*4,5-Dipropyl-1,3-dioxolan-2-one* (*VIa*). This was prepared much as above from *dl*-4,5-octanediol; it formed an oil; bp 105—110°C (bath temperature)/3 mmHg. IR (neat): 1802, 1180, 1030 cm^{-1}. NMR (CDCl$_3$): δ 0.8—2.2 (m, peak at δ 0.95 and 1.55, 14H, methyls and methylenes), 4.5—5.0 (m, 2H, CH–O). MS: *m/e* (relative abundance) 129 (4), 128 (3), 99 (5), 86 (10), 85 (12), 71 (28), 67 (36), 57 (78), 43 (100), 41 (98). Found: C, 62.9; H, 9.4%. Calcd for $C_9H_{16}O_3$: C, 62.8; H, 9.4%.

UV Irradiation of IIb in Isopropyl Alcohol-benzene. A mixture of IIb (0.42 g, 3 mmol), isopropyl alcohol (15 m*l*), and benzene (0.5 m*l*) was irradiated for 5 days. A subsequent GC of the mixture showed the presence of Vb and VIb, along with the recovered IIb. The separation of Vb and VIb was performed by preparative GC. The IR and mass spectra and retention times on the GC of both products were identical with those of the authentic samples. The yield of Vb and VIb was estimated by GC to be 13%, and the Vb/VIb ratio was determined to be 89:11.

cis- *and* trans-*4,5-Tetramethylene-1,3-dioxolan-2-one* (*Vb and VIb*).[21] These were prepared from *cis*- and *trans*-cyclohexane-1,2-diol much as has been described in the preparation of Va and VIa. The *cis* isomer, Vb, exhibited IR (neat): 1800, 1205, 1162, 1135, 1030 cm^{-1}. NMR (CDCl$_3$): δ 1.2—2.2 (m, 8H, methylenes), 4.5—5.0 (m, 2H, methines). The *trans* isomer, VIb, exhibited IR (Nujol): 1795, 1190, 1150, 1100, 1058, 1040 cm^{-1}. NMR (CDCl$_3$): δ 1.0—2.5 (m, 8H, methylenes), 3.8—4.3 (m, 2H, methines).

UV Irradiation of IIc. The irradiation of IIc (1.40 g, 8.3 mmol) in acetone for 6 days, and subsequent concentration and chromatography on a silica-gel column gave crystals (0.62 g, 44%); mp 268°C (acetonitrile-ethyl acetate (1:1)). IR (Nujol): 1805, 1190, 1050 cm^{-1}. NMR (CDCl$_3$): δ 0.8—2.8 (m, peak at δ 1.45, methylenes). MS: *m/e* (relative abundance) 168 (M$^+$/2, 61), 140 (9), 129 (14), 95 (35), 84 (62), 67 (48), 59 (76), 55 (89), 43 (100), 41 (73). Found: C, 64.1; H, 7.1%, MW (cryoscopic method) 325. Calcd for $C_{18}H_{24}O_6$: C, 64.3; H, 7.2%, MW 336.

The irradiation of IIc (1.01 g, 6 mmol) in isopropyl alcohol (18 m*l*) and benzene (1 m*l*) for 4 days, followed by the separation of the products by chromatography on a silica-gel column, gave the dimer in a 45% yield.

UV Irradiation of IId. An acetone solution (30 m*l*) of IId (1.00 g, 5.1 mmol) was irradiated for one day, then concentrated and subjected to chromatography on a silica-gel column. Elution with benzene gave the recovered IId (0.03 g) and an inseparable mixture of IX and X (0.71 g, 71%); bp 130—135°C/3 mmHg. IR (neat); 1800, 1175, 1160, 1028 cm^{-1}. NMR (CCl$_4$): δ 0.8—2.5 (m, peak at δ 1.80, 15H, methylenes and methine), 4.2—4.8 (m, 1H, CH–O). MS: *m/e* (relative abundance) 196 (M$^+$, 8), 152 (17), 124 (24), 110 (28), 109 (26), 97 (49), 95 (40), 84 (92), 81 (67), 67 (85), 55 (98), 41 (100). Found: C, 67.2; H, 8.0%. Calcd for $C_{11}H_{16}O_3$: C, 67.3; H, 8.2%.

Hydrolysis of IX and X. A mixture of IX and X (1.33 g, 6.8 mmol) was added to a solution of potassium hydroxide (1.5 g) dissolved in water (40 m*l*) and ethanol (40 m*l*). The whole was stirred for 6.5 hr at room temperature. The ethanol was then evaporated *in vacuo*, and residue was extracted with chloroform. The subsequent evaporation of the solvent and the purification of the residue by chromatography on a silica-gel column gave a mixture of XI and XII (0.83 g, 72%). The recrystallization of the mixture gave XI; mp 82—83°C (acetone). IR (Nujol): 3400, 1065, 1010, 910 cm^{-1}. NMR (CDCl$_3$): δ 0.8—2.3 (m, peak at δ 1.65, 15H, methylens and methine), 2.43 (s, 2H, OH), 3.2—3.8 (m, 1H, CH–O). MS: *m/e* (relative abundance) 170 (M$^+$, 6), 152 (9), 123 (15), 111 (17), 97 (100), 84 (66), 67 (29), 55 (41). Found:

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[21] P. Brown and C. Djerassi, *Tetrahedron*, **24**, 2949 (1968).

C, 70.5; H, 10.6%. Calcd for $C_{10}H_{18}O_2$: C, 70.5; H, 10.7%.

The plc of the mother liquid gave XII: bp 100—105°C/0.15 mmHg. IR (neat): 3480, 1085, 1035, 920 cm^{-1}. NMR ($CDCl_3$): δ 0.8—2.4 (m, 15H, methylenes and methine), 2.55 (s, 2H, OH), 3.0—3.7 (m, 1H, CH–O). MS: *m/e* (relative abundance) 170 (M$^+$, 12), 152 (12), 123 (15), 111 (34), 97 (100), 84 (70), 67 (33), 55 (50). Found: C, 70.5; H, 10.7%. Calcd for $C_{10}H_{18}O_2$: C, 70.5; H, 10.7%.

Oxidation of XI with NBS. A mixture of XI (0.14 g, 0.8 mmol), acetone (10 m*l*), water (1 m*l*), NBS (0.20 g, 1.1 mmol), and acetic acid (5 drops) was stirred overnight at room temperature. Subsequent work-up and purification by plc gave the ketol, XIII (0.07 g, 50%); bp 100°C (bath temperature)/3 mmHg. IR (neat): 3460, 1700, 1137 cm^{-1}. NMR ($CDCl_3$): δ 0.8—2.7 (m, peak at δ 1.75 and 2.25, methylenes and methine), 2.78 (s, 1H, OH). MS: *m/e* (relative abundance) 168 (M$^+$, 25), 150 (11), 124 (26), 111 (100), 98 (68), 97 (67), 83 (39), 78 (40), 55 (50). Found: C, 71.0; H, 9.6%. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6%.

Oxidation of XII with NBS. This was perfomed as has been described above. The IR and mass spectra and the retention time on GC were identical with those obtained by the oxidation of XI.

Reduction of XIII with VSH. A benzene solution of VSH (72 wt%, 0.5 m*l*) was added, drop by drop, to XIII (0.02 g, 0.12 mmol) in benzene (10 m*l*), and then the mixture was stirred overnight. A subsequent work-up gave diol (0.03 g, quantitative). The spectrum and retention time on the GC were identical with those of XI.

Periodate-permanganate Oxidation of XI and XII. To a mixture of XI and XII (0.36 g, 2.1 mmol), *t*-butyl alcohol (30 m*l*), potassium carbonate (0.10 g), and water (20 m*l*), we added an aqueous solution (50 m*l*) of sodium metaperiodate (2.60 g), potassium permanganate (0.05 g), and potassium carbonate (0.10 g) at room temperature; the mixture was then stirred for 3 hr. Extraction with chloroform and concentration gave the crude keto acid (XIV) (0.29 g, 78%). IR (neat): 3600—2400, 1735, 1710, 1200, 1155 cm^{-1}. MS: *m/e* (relative abundance) 184 (M$^+$, 4), 129 (14), 97 (16), 84 (100), 69 (24), 55 (50), 41 (58). The oxime melted at 121—124°C (lit,[14] 124—125.5°C). The semicarbazone melted at 192—193°C (lit,[14] 195—196°C).

Conversion of XI and XII to XV and XVI. A mixture of XI and XII (0.10 g, 0.6 mmol) and *p*-toluenesulfonyl chloride (0.12 g, 0.6 mmol) was treated with pyridine (5 m*l*) at room temperature, and stirring was continued overnight. A subsequent work-up gave the half-tosylate of XI and XII (0.15 g). IR (neat): 3420, 1170, 890 cm^{-1}.

The reduction of the half-tosylate with lithium aluminum hydride[22] or sodium borohydride[23] was performed according to the reported procedure. The GC of the mixture revealed the presence of XV as well as XVI, which was separated by preparative GC. The XVI alcohol showed IR (neat): 3380, 1140, 1035, 1015 cm^{-1}. MS: *m/e* (relative abundance) 154 (M$^+$, 7), 136 (100), 121 (35), 111 (33), 95 (55), 94 (58), 81 (50), 67 (83), 55 (60), 41 (73).

The attempted separation of XV was unsuccessful, but its formation was proven by comparing the retention times on two different GC columns (Dowfax 9N9, 10%, 2 m, and High Vacuum Silicone Grease, 10%, 2 m) with those of an authentic sample[24] which had been prepared by the hydroboration[25] of $\Delta^{1(7)}$-bicyclo[5.3.0]decene.[26] The XV alcohol thus obtained showed IR (neat): 3360, 1010 cm^{-1}. MS: *m/e* (relative abundance) 154 (M$^+$, 2), 136 (43), 121 (32), 97 (50), 95 (59), 81 (60), 67 (88), 55 (80), 41 (100).

UV Irradiation of IIe. The irradiation of IIe (4.29 g, 19 mmol) in acetone (60 m*l*) for 11 days and subsequent chromatography on a silica-gel column gave IIe (0.90 g, 21%) (elution with *n*-hexane–benzene (1:1)). Further elution with *n*-hexane–benzene (1:3) gave XIX (2.12 g, 49%). IR (neat): 1800, 1255, 1039 cm^{-1}. NMR (CCl_4): δ 1.2—2.8 (m, peak at δ 1.63, 19H, methylenes and methine), 4.0—4.7 (m, 1H, CH–O). MS: *m/e* (relative abundance) 224 (M$^+$, 9), 180 (3), 151 (6), 137 (6), 123 (14), 111 (24), 98 (66), 84 (52), 81 (49), 67 (63), 55 (100). Found: C, 69.5; H, 9.0%. Calcd for $C_{13}H_{20}O_3$: C, 69.6; H, 9.0%.

Hydrolysis of XIX. A mixture of XIX (2.12 g, 9.4 mmol), potassium hydroxide (2 g), water (40 m*l*), and ethanol (60 m*l*) was stirred overnight. A subsequent work-up gave crude XX (1.28 g, 69%). Recrystallization from *n*-hexane gave white needles; mp 90.4—91.6°C. IR (Nujol): 3360, 1094, 1015 cm^{-1}. NMR (CCl_4): δ 0.7—2.7 (m, 19H, methylenes and methine), 3.2—4.0 (m, 3H, CH–O and OH). MS: *m/e* (relative abundance) 198 (M$^+$, 10), 180 (4), 139 (12), 125 (27), 111 (19), 97 (93), 84 (100), 67 (57), 55 (90). Found: C, 72.7; H, 11.3%. Calcd for $C_{12}H_{22}O_2$: C, 72.7; H, 11.2%.

Oxidation of XX. This was performed much as has been described in the oxidation of XI and XII; it afforded XXI in an 86% yield. IR (neat): 3700—2300, 1737, 1708, 1410, 1250, 1200, 1155 cm^{-1}. MS: *m/e* (relative abundance 212 (M$^+$, 2), 163 (4), 123 (5), 109 (5), 97 (14), 84 (100), 83 (20), 69 (15), 55 (30). The semicarbazone melted at 169—171°C.

Hydrogenation of XXII. A mixture of XXII (0.13 g, 0.62 mmol) and Raney Nickel (*ca.* 0.1 g) in ethanol (10 m*l*) was stirred under a hydrogen atmosphere for a day. The subsequent filtration of the catalyst and concentration gave XXI quantitatively. The semicarbazone melted at 170—172°C.

UV Irradiation of IIf. A solution of IIf (2.5 g, 10.5 mmol) and iodine (0.2 g) in cyclohexane (75 m*l*) was irradiated for 7 days. The precipitates of XXIII (1.92 g, 77%) were collected by filtration and recrystallized from benzene to afford needles; mp 178—179°C. IR (KBr): 1840, 1805, 1622, 1605, 1120, 1045, 1024, 910, 740, 712 cm^{-1}. NMR ($CDCl_3$): δ 7.5—8.2 (m, 6H), 8.4—8.9 (m, 2H). MS: *m/e* (relative abundance) 236 (M$^+$, 80), 180 (44), 164 (100), 152 (28). UV (*n*-hexane): λ_{max} (log ε) 248 (5.72), 255 (5.82), 269 (4.95), 280 (4.67), 292 (4.86), 305 (5.12). Found: C, 76.1; H, 3.2%. Calcd for $C_{15}H_8O_3$: C, 76.3; H, 3.4%.

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