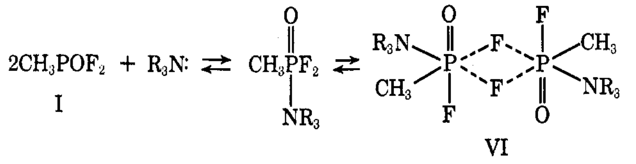
The lack of formation of IV in eq 2 and the stability of IV to reaction conditions may simply indicate that the mixed bridge is relatively unstable.[7] Some additional support for this view comes from the inability of chloride ion to readily displace fluoride ion from I in the presence of amine under our reaction conditions.

Our data support a labile complex between I and amines and also an exchange phenomenon; however, it does not appear that the complex is undergoing an intramolecular exchange. The results of our work seem to be best explained by rapid intermolecular exchange of fluorine *via* the fluorine bridged dimer shown in eq 5.



(5)

Experimental Section

Materials.—Methylphosphonic dichloride[8] and methylphosphonic difluoride[9] were prepared, distilled, and stored under dry nitrogen. The methylphosphonothioic difluoride was obtained from Ash-Stevens, Inc., under Contract No. DAAA15-69-C-0584. All amines were obtained from commercial sources and dried over CaO before use. Thiophene-free benzene from Mallinckrodt Chemical Works was distilled and dried over molecular seives.

Triethylammonium tosylate was prepared by adding triethylamine (0.1 mol) to toluenesulfonic acid (0.1 mol) dissolved in 50 ml of benzene. The solution was dried over anhydrous $MgSO_4$ and decanted into a dry flask, and the solvent was removed. The nmr spectrum of the solid which remained indicated that it was the desired tosylate. The compound was used without further purification.

Instruments.—The proton nmr spectra were recorded at 60 MHz using a Varian A-60D nmr spectrometer. The ^{19}F and ^{31}P studies were carried out at 94.1 and 40.5 MHz, respectively, using a Varian HA-100 nmr spectrometer. These spectra were obtained in the unlocked (HR) mode using the V-3507 unit to sweep the field.

Registry No.—I, 22382-13-4.

[7] Methylphosphonic chlorofluoride (IV) is stable to our reaction conditions.

[8] A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

[9] T. P. Dawson and K. C. Kennard, *J. Org. Chem.*, **22**, 1671 (1957).

Radiation-Induced and Electrochemical Formation of 3-Substituted 4,4-Dimethyl-γ-butyrolactone from α,β-Unsaturated Ester

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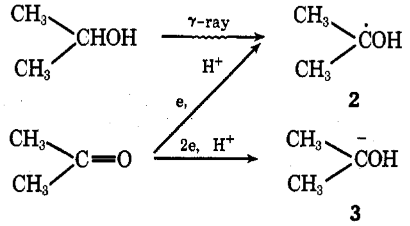
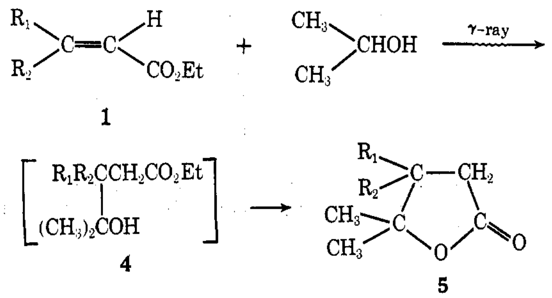
It has been previously reported[1] that radiation and ultraviolet-induced addition reactions of various alcohols to ethyl crotonate gave the corresponding 3-methyl-4-alkyl-substituted γ-butyrolactones. In the present paper, the radiation-induced addition reactions of 2-propanol and electrochemical reductive addition reactions of acetone to α,β-unsaturated esters are reported.

Since it is known that radiolysis of 2-propanol produces α-hydroxy radical **2**,[2-4] and electroreduction of acetone in a protic solvent gives radical **2** or anion **3**,[5-8] both addition reactions are expected to give the



identical products. In the present work, it was found that substituted γ-butyrolactones were obtained in fairly good yields by using such simple procedures.

Irradiation of α,β-unsaturated ester **1a–e** in a tenfold excess of 2-propanol with ^{60}Co γ-rays gave the corresponding 3-substituted 4,4-dimethyl-γ-butyrolactone **5a–e**.



a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = R_2 = CH_3$
d, $R_1 = H$; $R_2 = CO_2Et$
e, $R_1 = CO_2Et$; $R_2 = H$
f, $R_1 = C_6H_5$; $R_2 = H$

The yield of lactones, conversion of α,β-unsaturated esters, and *G* values of lactone formation and ester consumption are listed in Table I. *G* values were calculated from the low-conversion linear part of the curve which was obtained from the plot of the yield of lactone and the conversion of ester against the irradiation time.

Ethyl acrylate (**1a**) produced no lactone, probably because it easily polymerized by radical initiation. This is indicated by its high value of *G*(−**1a**).

Reactivity of the α,β-unsaturated ester toward the intermediate radical **6** seems to control the yield of lactone. A reactive ester such as **1a** proceeds predominantly in eq 2 to give a polymer, but in a less reactive ester an intermediate radical **6** may preferentially

[1] M. Tokuda, Y. Yokoyama, T. Taguchi, A. Suzuki, and M. Itoh, *J. Org. Chem.*, in press.

[2] W. R. McDonell and A. S. Newton, *J. Amer. Chem. Soc.*, **76**, 4651 (1954).

[3] (a) K. Hirota and M. Hatada, *Bull. Chem. Soc. Jap.*, **34**, 1644 (1961); (b) M. Hatada and K. Hirota, *ibid.*, **38**, 26 (1965).

[4] H. Muramatsu, K. Inukai, and T. Ueda, *ibid.*, **40**, 903 (1967), and references cited therein.

[5] F. D. Popp and H. P. Schultz, *Chem. Rev.*, **62**, 19 (1962).

[6] (a) T. Sekine, A. Yamura, and K. Sugino, *J. Electrochem. Soc.*, **112**, 439 (1965); (b) A. Yamura, T. Sekine, and K. Sugino, *J. Electrochem. Soc. Jap*, **34**, 110 (1966).

[7] K. Sugino and T. Nonaka, *J. Electrochem. Soc.*, **112**, 1241 (1965).

[8] K. Sugino and T. Nonaka, *Electrochim. Acta*, **13**, 613 (1968).

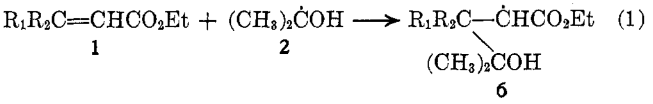
TABLE I

RADIATION-INDUCED ADDITION REACTION OF 2-PROPANOL TO α,β-UNSATURATED ESTER[a]

Compd	Yield of lactone **5**, %[b]	G(**5**)	Conversion of ester **1**, %[b]	G(−**1**)
1a	0	0	100	100
1b	44	8	86	19
c	41			
1c	29	5	64	10
1d	70	22	98	36
d	69			
1e	22	11	94	66
1f	0	0	35	4

[a] Irradiation time, 72 hr; dose rate, 8×10^5 r/hr; mole ratio of 2-propanol to ester, 10. [b] Based on α,β-unsaturated esters employed. [c] Instead of ethyl crotonate, crotonic acid was used. [d] Instead of ethyl maleate, maleic acid was used.

abstract a hydrogen from 2-propanol to form the γ-hydroxy ester **4** (eq 3). The interesting result is that



$$\underset{\mathbf{1}}{R_1R_2C{=}CHCO_2Et} + \underset{\mathbf{2}}{(CH_3)_2\dot{C}OH} \longrightarrow \underset{\mathbf{6}}{R_1R_2C(C(CH_3)_2OH){-}\dot{C}HCO_2Et} \quad (1)$$

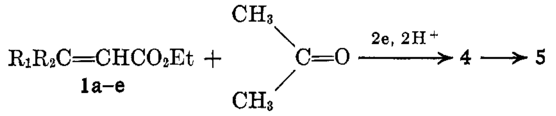
$$\mathbf{6} + n\underset{\mathbf{1}}{R_1R_2C{=}CHCO_2Et} \longrightarrow \text{telomer, polymer} \quad (2)$$

$$\mathbf{6} + (CH_3)_2CHOH \longrightarrow \mathbf{4} + \mathbf{2} \quad (3)$$

the G value of lactone formation was larger in diethyl maleate (**1d**) than the corresponding fumarate (**1e**) but the G value of ester consumption was about two times larger for diethyl fumarate. This is probably the result of trans olefin being more reactive towards radical addition than the cis isomer.[9] In support of this, Szwarc, *et al.*, report that the rate of methyl radical addition to diethyl fumarate is about six times faster than to diethyl maleate.[10] Also, the yield of 1:1 adduct in the radiation-induced addition of butyraldehyde to diethyl maleate is about three times larger than that to diethyl fumarate.[11] Since diethyl fumarate is more reactive toward radical addition, it would be consumed mainly in radical chain polymerization (eq 2), which results in the larger value of $G(-\mathbf{1})$. On the other hand, diethyl maleate would be mostly consumed in eq 3, resulting in the larger value of $G(\mathbf{5})$.

Irradiation of α,β-unsaturated acid, such as crotonic acid and maleic acid, produced γ-butyrolactone in almost the same yield as the corresponding esters.

When a mixture of α,β-unsaturated ester **1**, acetone, 20% sulfuric acid, and water was electrolyzed for 1 hr with a terminal voltage of 75–95 V, Michael-type addition of anion **3** to α,β-unsaturated ester occurred to give γ-lactone through the intermediate ester **4**. The electrode employed was a mercury pool (cathode) and a platinum plate (anode), and the procedure for electrolysis was simplified with no partition between the cathode and the anode chamber. The yield of lactone **5**, the conversion of ester **1**, and its reaction conditions are summarized in Table II.



$$\underset{\mathbf{1a\text{–}e}}{R_1R_2C{=}CHCO_2Et} + (CH_3)_2C{=}O \xrightarrow{2e,\ 2H^+} \mathbf{4} \longrightarrow \mathbf{5}$$

TABLE II

ELECTROCHEMICAL ADDITION REACTION OF ACETONE TO α,β-UNSATURATED ESTER[a]

	Substrate							
Compd	Ester, g	Acetone, ml	20% H_2SO_4, ml	H_2O, ml	Terminal voltage, V	Current, A	Yield of lactone **5**, %[b]	Conversion of ester **1**, %[b]
1a	1.0	20	0.83	2	90	0.9	95	100
1b	1.0	20	0.83	2	90	0.9	30	60
c	1.0	20	0.83	5	80	1.3	36	
1c	1.0	20	0.83	2	93	0.8	Trace	30
1d	1.0	20	0.83	0	85	1.0	59	100
	1.0	20	0.83	5	80	1.2	Trace[d]	100
1e	1.0	20	3.30	0	75	1.5–2.0	21	100
	1.0	20	0.83	5	80	1.3	8[e]	100
1f	1.0	20	1.66	0	83	1.0	0	

[a] Electrolysis was conducted under the above conditions for 1 hr. [b] Based upon ester employed. [c] Instead of ester, crotonic acid was used. [d] Diethyl succinate was produced in 95% yield. [e] Diethyl succinate was produced in 90% yield.

The remarkable difference between the radiation-induced and the electrochemical addition reactions was that in the latter case 4,4-dimethyl-γ-butyrolactone (**5a**) was obtained in an almost quantitative yield. From this result, it is suggested that the reactive species in the electrolysis is not a radical **2** but an anion **3**, as Sugino, *et al.*,[8] have already pointed out. The yield of lactone is gradually decreased as alkyl substitution at the β position of α,β-unsaturated ester increases.

In the case of diethyl maleate (**1d**) and diethyl fumarate (**1e**), ethyl 2,2-dimethylparaconate (**5d**) was obtained in yields of 59 and 21%, respectively, but in some conditions an electrolytic reduction of ester took place to produce diethyl succinate.

Experimental Section

Gas–liquid chromatographic analyses were carried out with a Yanagimoto Model GCG-550 and preparative work was done with a Varian Autoprep 700. Infrared spectra were obtained with a Hitachi EPI-G22, and nuclear magnetic resonance spectra were measured with a JEOL 3H-60 (tetramethylsilane as the internal standard). Mass spectra were obtained with a Hitachi RMU-6E. Quantitative glpc analyses were carried out by an

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(9) W. A. Pryor, "Free Radical", McGraw-Hill, New York, N. Y., 1966, p 223

(10) (a) A. R. Barder, R. P. Buckly, F. Leavitt, and M. Szwarc, *J. Amer. Chem. Soc.*, **79**, 5621 (1957); (b) M. Szwarc and J. H. Binks in "Theoretical Organic Chemistry, The Kekule Symposium," Butterworths, London, 1958, p 278.

(11) R. H. Wiley and J. R. Harrell, *J. Org. Chem.*, **25**, 903 (1960).

internal standard method. All melting points and boiling points are uncorrected.

All reagents were distilled or recrystallized before use. Ethyl crotonate, ethyl β,β-dimethylacrylate, diethyl maleate, diethyl fumarate, and ethyl cinnamate were prepared by esterification of the corresponding acids. β,β-Dimethylacrylic acid was prepared by the procedure reported by Smith, *et al.*[12] 2-Propanol was dried over calcium oxide and acetone was distilled in the presence of magnesium. Mercury was purified with dilute nitric acid.

General Procedure for Radiation-Induced Reaction.—The general procedure was carried out by the method previously reported.[1] For glpc analyses, a 15% FFAP (Free Fatty Acid Polyester) column coated on Diasolid M (Nihon Chromato Work, Ltd.) and a 15% Apieson Grease L column coated on Diasolid L were used at 150–240° with 4-*tert*-butyltoluene and diethyl phthalate as the internal standard.

General Procedure for Electrochemical Reaction.—The electrochemical cell used was a cylindrical vessel, 3 cm in diameter and 15 cm in height, with no partition between the cathode and the anode chamber. The reaction vessel was cooled with running water throughout the electrolysis. The mercury pool (55 g) at the bottom of the cell was used as the cathode. The anode was a platinum plate (1 × 1 cm^2), which was held 1 cm apart from the mercury electrode.

A typical procedure is as follows: a mixture of α,β-unsaturated ester (1 g), acetone (20 ml), 20% sulfuric acid (0.8–3.3 ml), and water (0–5 ml) was electrolyzed for 1 hr with a terminal voltage of 75–95 V at a current of 0.35–1.6 A, and then the resultant mixture was neutralized with a 5% NaOH solution and extracted with ether. The ether solution was analyzed by glpc.

Analysis of Products.—A product was separated by a distillation and a preparative glpc (silicone gum rubber SE-30 or Apieson Grease L), and identified from ir, nmr and mass spectral data. Physical properties are summarized in Table III.

TABLE III

PROPERTIES OF γ-BUTYROLACTONES

Compd	Bp, °C (mm)	*n*D (°C)	Found, %		Calcd, %	
			C	H	C	H
5a	110.5–111.5 (45)[a]	1.4352 (15)[b]	62.95	8.79	63.13	8.83
5b	97 (15)[c]	1.4373 (20)[d]	65.32	9.48	65.59	9.44
5c	100–103 (17) mp 100–101.5[e]		67.30	9.85	67.57	9.93
5d	138–140 (8)	1.4445 (25)	58.26	7.71	58.05	7.58
f	mp 174–175[g]		53.05	6.35	53.16	6.37

[a] Lit. bp 201–206° (760 mm): R. T. Arnold, J. S. Buckley, Jr., and J. Richter, *J. Amer. Chem. Soc.*, **69**, 2322 (1947). Lit. bp 89–91° (17 mm): R. L. Frank, R. Armstrong, J. Kwiatek, and H. A. Price, *ibid.*, **70**, 1379 (1948). [b] Lit. *n*D 1.4352 (20°): *ibid.*, **70**, 1379 (1948). [c] Lit. bp 216–217° (744 mm): J. W. Huffman and J. W. Bethea, *J. Org. Chem.*, **30**, 2956 (1965). [d] Lit. *n*D 1.4402 (17°): M. Pfau, R. Dulou, and M. Vilkas, *C. R. Acad. Sci.*, **251**, 2188 (1960). [e] Lit. mp 99–100°: A. W. Burgstahler and D. E. Wetmore, *J. Org. Chem.*, **26**, 3516 (1961). [f] 2,2-Dimethylparaconic acid. [g] Lit. mp 176°: G. O. Schenck, G. Koltzenburg, and H. Grossmann, *Angew. Chem.*, **69**, 177 (1957). Lit. mp 174°: J. F. Laporte and R. Rambaud, *C. R Acad. Sci., Ser. C*, **262**, 1095 (1966).

Registry No.—**1a**, 140-88-5; **1b**, 623-70-1; **1c**, 638-10-8; **1d**, 141-05-9; **1e**, 623-91-6; **1f**, 4192-77-2; **5a**, 3123-97-5; **5b**, 2981-96-6; **5c**, 16466-24-3; **5d**, 34566-25-1; 2-propanol, 67-63-0; 2,2-dimethylparaconic acid, 79-91-4.

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[12] L. I. Smith, W. W. Prichard, and L. J. Spillance, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 302.

The Synthesis of 2,2,5-Trimethyl-6-hydroxy-2*H*-naphtho[1,2-*b*]pyran and 2-(γ,γ-Dimethylallyl)-3-methylnaphthoquinone. A New Route to Naphthopyrans and the Vitamin K$_1$ Series

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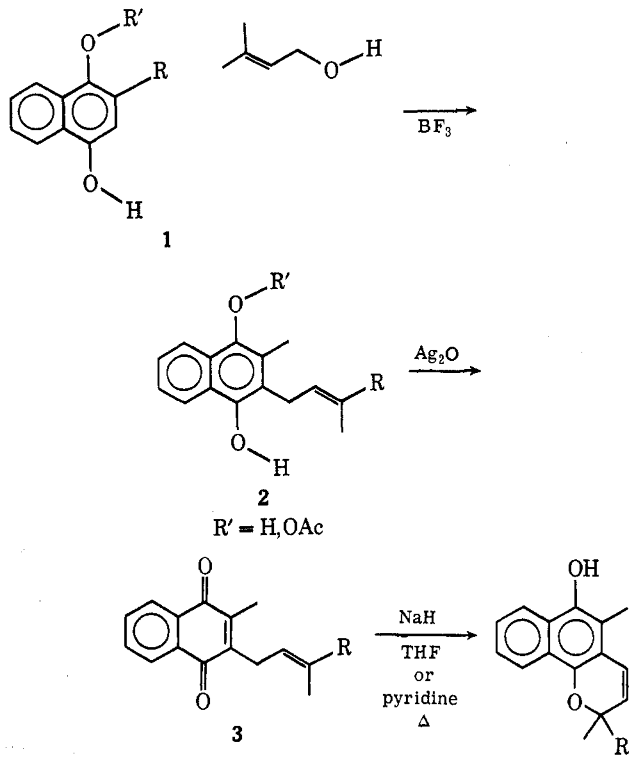
In connection with an investigation of possible intermediates in oxidative phosphorylation, a moderately large quantity of the naphthopyranol **11** and its acetate ester **8** and methyl ether **10** derivatives were desired. A literature search divulged no specific preparations of these compounds but did suggest several possible general approaches. Alkylation of menadiol or of menadiol-1-acetate (**1**) by allylic alcohols, catalyzed by boron trifluoride,[1] affords intermediates **2** which can be oxidized to quinones **3** and then cyclized to the desired naphthopyranol system by sodium hydride–THF[2] or pyridine[3] (Scheme I). These alkylations suffer, however, from the necessity of using large excesses of **1** to achieve good yields. Yields in the alkylation step are typically 20–40%[4] and conversions range from minute to about 20%. Although the oxidation step is quite efficient, yields in the subsequent cyclization are not

SCHEME I



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[1] R. Hirschmann, R. Miller, and N. L. Wendler, *J. Amer. Chem. Soc.*, **76**, 4592 (1954).

[2] A. Wagner, D. Wittreich, B. Arison, N. Trenner, and K. Folkers, *ibid.*, **85**, 1178 (1963).

[3] D. McHale and J. Green, *Chem. Ind.* (*London*), 1867 (1962).

[4] (a) C. C. Lee, F. C. G. Hoskin, L. W. Trevoy, L. B. Jaques, and J. W. Spinks, *Can. J. Chem.*, **31**, 769 (1953); (b) O. Isler and K. Doebel, *Helv. Chim. Acta*, **27**, 225 (1954).