portion of the mixture with 10 mL of 10% H_2SO_4 for 2 h gave 0.7 g of **1**.

Carbonylation of 1-Chloro-2-butene. Distillation of the crude product mixture gave 1,3-dichlorobutane (8.8 g, 23%) and γ-valerolactone (4.8 g, 16%). NMR and IR spectra of these samples were identical with those of commercial materials.

Carbonylation of Methallyl Methyl Carbonate. Bulb-to-bulb distillation (100 °C bath, 25 mmHg) gave 3,3-dimethylpropiolactone (4.5 g, 15%): ^1H NMR ($CDCl_3$) δ 4.05 (s, 2 H), 1.48 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 154.5 (C=O), 81.7 (C-3), 75.2 (C-4), 25.8 (Me); IR (neat) 1800 cm^{-1}; MS, $(m + 1)/z$ 101 (M^+), 57 ($M^+ - CO_2$).

Preparation of Carbonates. The carbonates were prepared by the treatment of a mixture of the appropriate allyl alcohol and methyl chloroformate with triethylamine at 0 °C: allyl methyl carbonate, bp 127.5–128 °C; methallyl methyl carbonate, bp 148–149 °C.

Registry No. **1**, 35594-14-0; **2**, 123-15-9; **3**, 103564-35-8; **4**, 103564-36-9; **10**, 108-29-2; $H_3CCHClCH_2CH_2Cl$, 1190-22-3; $H_2C{=}CHCH_2OCOOMe$, 35466-83-2; $H_2C{=}C(CH_3)CH_2OCOOMe$, 81112-28-9; H_2SO_4, 7664-93-9; $H_2C{=}CHCH_2OH$, 107-18-6; $H_2C{=}C(CH_3)CH_2OH$, 513-42-8; ClCOOMe, 79-22-1; $H_2C{=}CHCH_2OMe$, 627-40-7; $H_2C{=}CHCH_2CHO$, 7319-38-2; $H_3CCH(OH)CH_2OH$, 57-55-6; $H_3CCH(OH)CH_2Cl$, 127-00-4; $H_2C{=}CHCH_2Cl$, 107-05-1; $H_3CCH{=}CHCH_2Cl$, 591-97-9; $H_3CCHClCH{=}CH_2$, 563-52-0; $H_2C{=}CHCH(OMe)CH_3$, 17351-24-5; CO, 630-08-0; 3,3-dimethylpropiolactone, 1955-45-9.

Carbonylation of Aldehydes in Strong Acid. A General Synthesis of 3,4-Dialkyl-2(5*H*)-furanones

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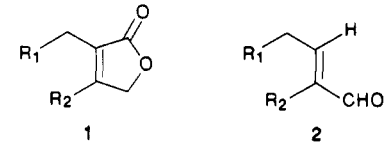
The carbonylation of organic compounds in a strongly acidic medium is a versatile synthetic tool[2] providing easy access to tertiary carboxylic acids and esters under relatively mild conditions from olefins and alcohols.[3,4] Although simple aldehydes, such as formaldehyde and acetaldehyde, are known to react normally to yield 2-hydroxyalkanoic acids,[5,6] extension to higher or more complex aldehydes is lacking.[7] In the preceding paper we presented the unusual conversion of allylic compounds to lactones. Most unexpected is the formation of 3-ethyl-4-methyl-2(5*H*)-furanone (**1b**) from allyl methyl carbonate,[8] presumably via the intermediacy of 2-methyl-2-pentenal (**2b**). In this paper, we report on the transformation of α,β-unsaturated aldehydes to 3,4-dialkyl-2(5*H*)-furanones and a one-step procedure to the same products via the carbonylation of *n*-alkanals.

The addition of an α,β-unsaturated aldehyde to an autoclave previously charged with concentrated sulfuric acid and CO (6.9 MPa) at 50 °C and quenching the reaction with water gave **1** (Table I). Alternatively, α,β-unsaturated aldehydes may be formed in situ from *n*-alkanals,

Table I. Carbonylation of Aldehydes

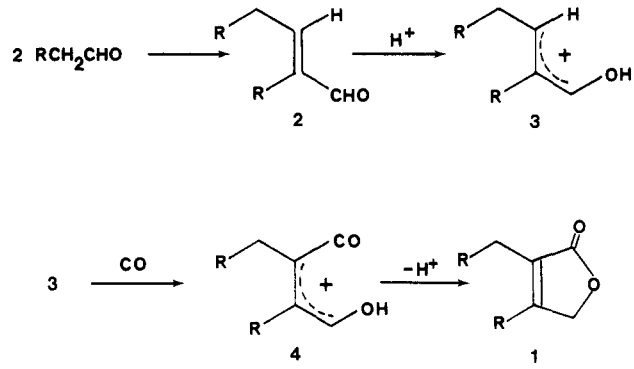


1 **2**

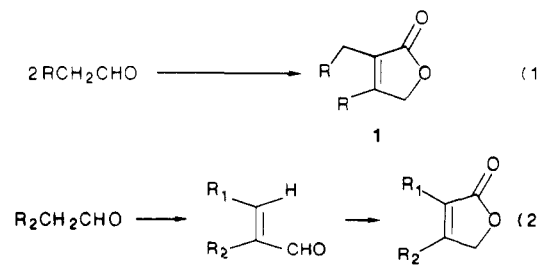
a: R_1 = H, R_2 = CH_3
b: R_1 = R_2 = CH_3
c: R_1 = R_2 = Et
d: R_1 = R_2 = *n*-pentyl

aldehyde	product	yield, %
EtCHO	**1b**	44
n-PrCHO	**1c**	38.5
n-$C_6H_{13}CHO$	**1d**	24.0
2a	**1a**	54.6
2b	**1b**	52.0
2c	**1c**	43.0

Scheme I



which then undergo carbonylation to identical products. Although this one-step procedure is more convenient, it imposes a restriction on the structures of the furanones to those in which the 3-alkyl substituents are always the next higher homologues of the 4-alkyl groups (eq 1). On the other hand, there is not such restriction with preformed α,β-unsaturated aldehydes. Thus, aldol condensation of ethanal and *n*-propanal gave 2-methyl-2-butenal (**2a**), which was carbonylated to 3,4-dimethyl-2(5*H*)-furanone (**1a**) in 54.6% yield. Since a large number of α,β-unsaturated aldehydes can be obtained by aldol condensation, this method constitutes a versatile synthesis of furanones (eq 2).



Acrolein and mesityl oxide, however, did not give any identifiable products. Branched alkanals also failed in this reaction because of the inability of the intermediate aldols to undergo dehydration. The only product observed in the reaction of 2-methylpropanal was the oxidized material, 2-methylpropanoic acid.

These results can be rationalized by the reaction sequence depicted in Scheme I. The aldol condensation of aldehydes in acidic media to α,β-unsaturated aldehydes is well documented.[9] The carbonylation of **3** from the

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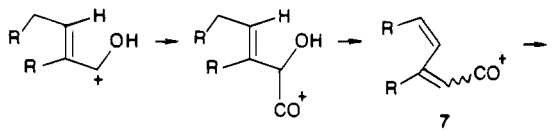
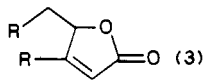
protonation of **2** yields **4**, which then cyclizes to **1**. The regioselectivity of CO incorporation is rather puzzling. In principle, both termini of **3** can react with CO. Reaction at the aldehydic carbon should lead to the isomeric **5** (eq 3). Since an α-OH group is supposed to stabilize a carbenium ion,[10] **5** may be expected to be the major product on the basis that Koch reaction products are generally determined by the relative stabilities of the intermediate carbenium ions. However, **5** was not observed in any of the reactions studied. It is, of course, possible that carbonylation is reversible and that **6** is less thermodynamically stable than **4** or either **6** or **7** is unstable under the reaction conditions. The real cause for the absence of **5** will have to await further study.



6 **7**



5 (3)

2(5*H*)-Furanones occur as natural products[11] and are versatile synthetic intermediates since, e.g., they react readily as Michael acceptors[12] and can be reduced to furans.[13,14] A large body of literature is available on the synthesis of these compounds,[15] but none is comparable to our method with respect to simplicity and availability of starting materials.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Varian EM360 or a JEOL FX90 spectrometer. Infrared spectra were recorded on a Beckmann AccuLab instrument. Mass spectra were obtained by use of a Finnigan 4000 GC/MS system operating in the chemical ionization mode with methane. Gas chromatographic analysis utilized a Hewlett-Packard 5700A instrument with 6 ft $\times$ $^1/_8$ in. columns packed with 5% Carbowax 20M or SE 30. Elemental analyses were performed by the Analytical Laboratories, Michigan Division, The Dow Chemical Co.

General Method. All reactions were run under identical conditions and are illustrated by the procedure for the carbonylation of *n*-propanal. Sulfuric acid (96%, 100 mL, 1.81 mol) was placed in a 300-mL stainless steel autoclave equipped with a high-speed stirrer and heated to 50 °C. After the vessel was closed and flushed with nitrogen, carbon monoxide was introduced until the pressure reached 6.9 MPa. With stirring at 1700 rpm, *n*-propanal (17.4 g, 0.3 mol) was added at a rate of 0.15 mol per hour by means of a modified HPLC pump. Stirring and heating were continued for 2 more h after all the aldehyde had been added. The vessel was then cooled to room temperature and the excess carbon monoxide vented. The contents were cautiously added to 200 g of ice. The aqueous solution was saturated with ammonium chloride and extracted with ether (2 $\times$ 300 mL). After the mixture was dried with anhydrous $MgSO_4$, the solvent was removed on a rotary evaporator at room temperature and the resulting residue distilled at reduced pressures to give **1b** (8.32 g, 44%): bp 100–103 °C (10 mmHg) [lit.[16] bp 112–118 (12 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 4.63 (s, 2 H), 2.30 (q, 2 H, J = 7.0 Hz), 2.05 (s, 2 H), 1.1 (t, 3 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 174.6 (C=O), 155.8 (C-3), 128.7 (C-4), 72.4 (C-5), 16.7, 12.6, 12.0 (Et, Me); IR (neat) 1750, 1680 cm^{-1}; MS, $(m + 1)/z$ 127 (M).

3-*n*-Propyl-4-ethyl-2(5*H*)-furanone (1c). The carbonylation of *n*-butanal (21.6 g, 0.3 mol) gave 8.9 g (38.5%) of **1c**: bp 125–130 °C (12 mmHg); ^{1}H NMR ($CDCl_3$) δ 4.76 (s, 2 H), 2.38 (m, 4 H), 1.52 (m, 2 H), 1.03 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 175.1, 161.9, 126.2, 70.7, 25.3, 21.3, 20.2, 13.7, 12.2; IR (neat) 1750, 1670 cm^{-1}; MS, $(m + 1)/z$ = 155 (M). Anal. Calcd for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found: C, 70.35; H, 9.11.

3-*n*-Hexyl-4-*n*-pentyl-2(5*H*)-furanone (1d). From *n*-heptanal (34.2 g, 0.3 mol) was obtained 8.6 g (24%) of **1d**: bp 142–146 °C (1 mmHg); ^{1}H NMR ($CDCl_3$) δ 4.55 (s, 2 H), 2.26 (m, 4 H), 1.31 (m, 14 H), 0.89 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 175.09, 160.51, 127.09, 71.13, 31.63, 31.52, 29.14, 28.06, 27.57, 27.03, 23.56, 22.53, 13.97, 13.81; MS $(m + 1)/z$ = 239 (M). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.63; H, 10.92. Found: C, 75.90; H, 10.71.

3,4-Dimethyl-2(5*H*)-furanone (1a). The carbonylation of 2-methyl-2-butenal[9] gave 54.6% of **1a**: bp 99–102 °C (10 mmHg) [lit.[16] bp 103–112 °C (14 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 4.51 (s, 2 H), 2.00 (s, 3 H), 1.81 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 175.1, 156.4, 122.5, 72.3, 11.9, 7.9.

Registry No. **1a**, 1575-46-8; **1b**, 35594-14-0; **1c**, 103563-97-9; **1d**, 103563-98-0; **2a**, 1115-11-3; **2b**, 623-36-9; **2c**, 64344-45-2; CH_3CH_2CHO, 123-38-6; $CH_3(CH_2)_2CHO$, 123-72-8; $CH_3(CH_2)_5CHO$, 111-71-7; H_2SO_4, 7664-93-9; CO, 630-08-0.

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Aryl-Activated Carbon–Chlorine Bond Cleavage at the Bridgehead Positions in 1-Chloro- and 1,4-Dichloro-7,7-dimethoxybenzonorbornene[1]

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There have been several reports of the photolytic cleavage of bridgehead iodides by direct photolysis of the carbon–halogen chromophore.[2] The cleavage of simple benzylic systems (such as benzyl chloride), through light absorbed by the aromatic ring, has also been extensively studied.[3] Our own interest has been in the photochemical intramolecular activation of remote (frequently UV transparent) functional groups,[1,4] and, in this context, we noted calculations[5] that indicated significant $\pi,\pi^*/\sigma,\sigma^*$ interaction[1,6] might occur in a bridgehead-substituted benzonorbornene. This suggested one might observe photolytic cleavage of a 1-chlorobenzonorbornene derivative despite the unfavorable location of the halogen.

As a prototypical example, we prepared 1,4-dichloro-7,7-dimethoxybenzonorbornene (**1**) by using published

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