579-44-2; 8, 94-02-0; $ClCO_2CH_2Ph$, 501-53-1; H_2O_2, 7722-84-1; $PhCH_2COCl$, 103-80-0; (±)-$PhCH(OH)CO_2H$, 611-72-3; (±)-$PhCH(CO_2H)OCO_2CH_2Ph$, 103423-01-4; (*R*)-$PhCH(OH)CO_2H$, 611-71-2; (±)-$PhCH(COCl)OCO_2CH_2Ph$, 103423-05-8; (*R*)-4-isopropyloxazolidin-2-one, 95530-58-8.

Carbonylation in Strong Acid. Lactones from Allylic Derivatives

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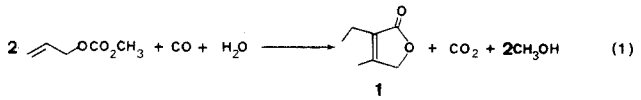
Received September 16, 1985

The carbonylation of organic compounds with carbon monoxide in the presence of a soluble transition-metal catalyst, particularly of group VIII, has been an area of great interest and has provided access to many valuable products.[2] However, carbonylation in strong acid has received much less attention even though it is practiced in the commercial production of pivalic and other alkanoic acids.[3] In the Koch modification, the substrate is mixed with a strong acid under a moderate carbon monoxide pressure in the absence of water to generate an intermediate acylium ion which is then carefully hydrolyzed.[4] The reaction conditions are surprisingly mild in comparison to metal-catalyzed reactions. Typically, temperatures between −20 and 80 °C and pressures less than 10 MPa are employed. Strong acids such as H_2SO_4, H_3PO_4, HF, and BF_3 are used as the catalysts as well as the solvents. Under these conditions, nearly all olefins and a number of dienes, unsaturated esters, alcohols, diols, reactive alicyclic compounds, halogenated compounds, certain amines, and esters react to form the corresponding carboxylic acids.[5]

In general, the products of the Koch reaction are determined by the relative stabilities of the carbenium ions from protonation of the substrates. With higher olefins and alcohols, rearrangement, disproportionation, and dimerization can occur leading to mixtures of products. Only a very limited number of examples of substituted olefins have been reported, and the products observed are predictable. β-Citronellyl chloride and methallyl chloride gave 2,2,6-trimethyl-8-chloro-1-octanoic acid and chloropivalic acid, respectively.[6] Our effort has been focused on the carbonylation of oxysubstituted allylic compounds, the results of which are reported herein.

The gradual introduction of allyl methyl carbonate into a pressure vessel containing concentrated sulfuric acid and pressurized with CO (6.9 MPa) maintained at 50 °C followed by cautious discharge of the solution into ice–water gave 3-ethyl-4-methyl-2(5*H*)-furanone (**1**) in 48% distilled yield and a considerable amount of tar (eq 1).

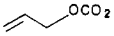
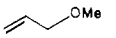
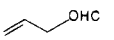
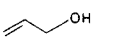
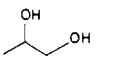
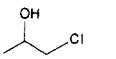
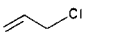


(1)

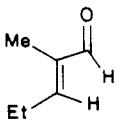
1

Other allylic compounds also provided **1**, albeit in lower yields (Table I). When 1,2-propanediol, 1-chloro-2-propanol, or allyl chloride were used, additional products (11.4% of **2** from the diol and 30% of a mixture of **3** and **4** from the others) were isolated along with **1**.

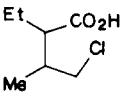
Table I. Yield of 1 from Carbonylation of C_3 Derivatives[a]

C_3 derivative	product 1, %	product other (%)
	48	
	28	
	18.5	
	20	
	19	2 (11.4)
	10	3 + 4 (30)
	10	3 + 4 (30)

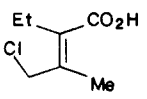
[a] Substrate:H_2SO_4 = 1:6.



2



3



4

The identities of **1** and **2** were established by comparison with authentic samples[7,8] and those of **3** and **4** by inference from their solubility in base, spectral data, and their conversion to **1** in hot aqueous acid.

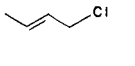
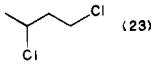
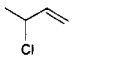
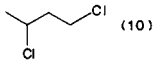
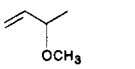
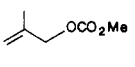
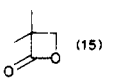
The C_7 skeleton common to all the products can only be satisfied by a dimerization of allylic fragments and CO incorporation, in a manner similar to the formation of C_9 and C_{13} acids from isobutylene via acid-catalyzed dimerization and trimerization.[9] In our case, the product is more complex, and its formation cannot be readily rationalized on the basis of the known reaction sequence. The observation of the same product from all the C_3 derivatives and the isolation of **2-4**, which we believe are closely related and are intermediates to **1**, suggest that the pathway outlined in Scheme I is operative. The formation of allyl carbenium ion from the starting materials in concentrated sulfuric acid is expected.[10] Addition of an allyl cation to another allylic molecule followed by proton loss and rearrangement gives the conjugated diene **5**. The C_6 allyl cation, from the protonation of **5**, reacts with CO to yield an acylium complex **7**[11] which upon hydrolysis gives the acid **8**. The final product, **1**, results from the acid-catalyzed ring closure of **8**. It can be seen that **5** is equivalent to the enol form of **2** and that **8** is identical with **3** and **4** when Y = Cl, thus accounting for all the products observed. The intermediacy of **2** is supported by the observation that it was the sole product when the carbonylation of 1,2-propanediol was conducted at 20 °C.

The difference in yields from the various allylic compounds is difficult to explain and may be related to their relative stabilities in sulfuric acid. The predominance of **3** and **4** in the reaction products of 1-chloro-2-propanol and allyl chloride is probably due to the slower rate at which they cyclize to **1** as compared to the rate for the oxygen analogues. To confirm the fast cyclization of the latter, **1** was hydrolyzed by sodium hydroxide to **9**, and the pH of the solution was the adjusted to 3 and 5.6 with aqueous HCl or ammonium sulfate at room temperature. Moni-

(1) Address correspondence to: The Dow Chemical Company, M. E. Pruitt Building, Midland, MI 48674.
(2) *Organic Synthesis via Metal Carbonyls*; Wender, I.; Pino, P.; Eds.; Wiley: New York, 1977; Vol. 2.
(3) Ellis, W. J.; Roming, C., Jr. *Hydrocarbon Process.* **1965**, *44*, 139.
(4) Koch, H.; Gilfert, W. *Brennst.-Chem.* **1955**, *36*, 321.
(5) Bahrman, A. *New Synthesis with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: West Berlin, 1980; p 372.
(6) Möller, K. E. *Brennst.-Chem.* **1966**, *47*, 10.
(7) Duenger, M. Ger. Offen. 2 154 439, 1971.
(8) Green, M. B.; Hickinbottom, W. J. *J. Chem. Soc.* **1957**, 3262.
(9) Koch, H.; Möller, K. E. Ger. Offen. 1 095 802, 1959.

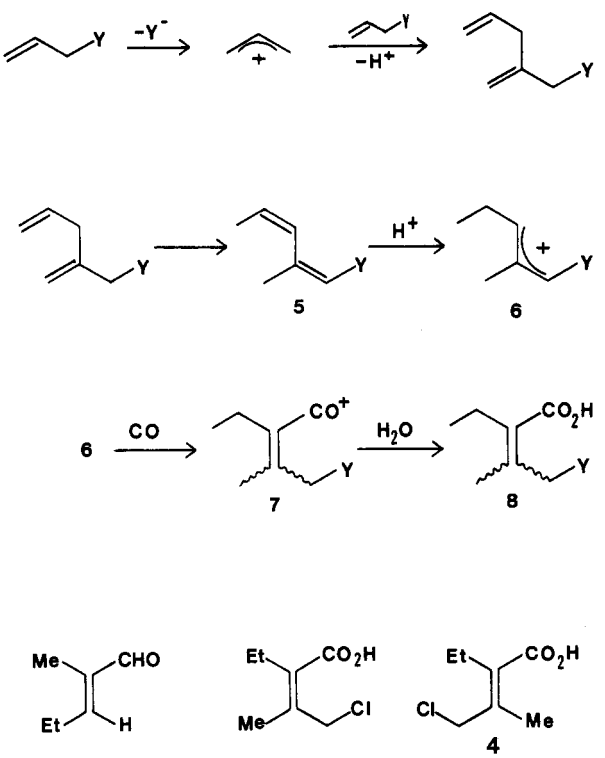
0022-3263/86/1951-3704$01.50/0

Table II. Carbonylation of C_4 Allyl Derivatives[a]

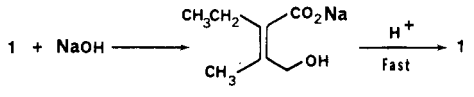
starting material	product (% yield)	
	**10** (16)	 (23)
	**10** (10.5)	 (10)
	**10** (17)	
	 (15)	

[a] Substrate:H_2SO_4 = 1:6.

Scheme I

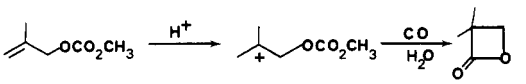


toring the appearance of 1 showed that about 50% was formed almost immediately upon mixing and >90% in 30 min at the lower pH. At the higher pH, the rate was substantially slower (eq 2).



(2)

Under the same carbonylation conditions, 1-chloro-2-butene surprisingly gave γ-valerolactone (**10**) and 1,3-dichlorobutane. Two other C_4 allyl derivatives behaved similarly (Table II). Unexpectedly, methallyl methyl carbonate did not react via the allylic carbenium ion as evidenced by the formation of 3,3-dimethylpropiolactone[12] (eq 3). In this case, protonation of the double bond to a tertiary carbenium ion was preferred over ionization to the allylic cation.



(3)

The absence of dimerization products from C_4 allylic derivatives may be attributed to the difference in stability between the corresponding allyl cations: the more stable C_4 cations apparently react with CO before dimerization. The valerolactone and propiolactone are results of cyclization of the initially formed unsaturated acids; 1,3-dichlorobutene is the result of HCl addition to the starting materials.

No attempts have been made to optimize these carbonylation reactions since the intent of this work was of a screening nature. Sulfuric acid, although convenient, is probably not the solvent of choice for obtaining high yields. Nevertheless, the isolated yield of up to 48% attests to the stability of **1**. This work has added a new dimension to the Koch reaction and highlighted its synthetic potential, the further exploration of which is reported in the accompanying paper.

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 × $^1/_8$ in. columns packed with 5% Carbowax 20M or SE 30.

General Method. All reactions were run under identical conditions and are illustrated by the procedure for the carbonylation of allyl methyl carbonate. 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, allyl methyl carbonate (34.8 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 two more hours after all the carbonate 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 × 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 **1** (9.2 g 48%): bp 100–103 °C (10 mmHg) [lit.[7] bp 112–118 °C (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 174.9 (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^+).

Carbonylation of 1,2-Propanediol. With the procedure above, 1,2-propanediol (22.8 g, 0.3 mol) was carbonylated. The crude product mixture gave **2** upon distillation (1.7 g, 11.4%) [bp 35–37 °C (20 mmHg) (lit.[8] bp 38–39 °C (25 mmHg))] and **1** (3.62 g, 19%) [bp 110–115 °C (20 mmHg)]. **2**: ^{1}H NMR ($CDCl_3$) δ 9.37 (s, 1 H), 6.48 (t, 1 H), 2.35 (m, 2 H), 1.71 (s, 3 H), 1.10 (t, 3 H), ^{13}C NMR δ 195.3, 156.2, 138.8, 22.3, 12.8, 9.0. Spectral data were identical with those of an authentic sample.[8]

Carbonylation of Allyl Chloride. The crude product from the carbonylation of allyl chloride (23.0 g, 0.3 mol) was first extracted with a solution of 5% NaOH. The ether layer gave 1.9 g (10%) of **1**. Acidification of the aqueous layer yielded 7.4 g (30%) of a mixture of **3** and **4** as an oil: MS, (m + 1)/z 163, 165, (M^+), 127 (M^+ – Cl); IR (neat) 3450, 1760 cm^{-1}. Refluxing a 1-g

(10) Noble, W. J. *Highlights of Organic Chemistry*; Marcel Dekker: New York, 1974; p 699.

(11) The exact locations of the double bonds in all the intermediates are of little significance since rapid equilibration is expected in the strongly acidic medium.

(12) The ^{1}H NMR spectrum [δ 4.05 (s, 2 H), 1.48 (s, 6 H)] rules out the possibility of the other isomer, 4,4-dimethylpropiolactone. The IR absorption at 1800 cm^{-1} is indicative of a four-membered ring, confirmed by the ^{13}C NMR carbonyl peak at 154.5 ppm (154.6 ppm reported for 3-allypropiolactone by Cowell and Stille[13]).

(13) Cowell, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4193.

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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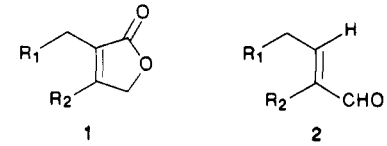
Received September 16, 1985

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

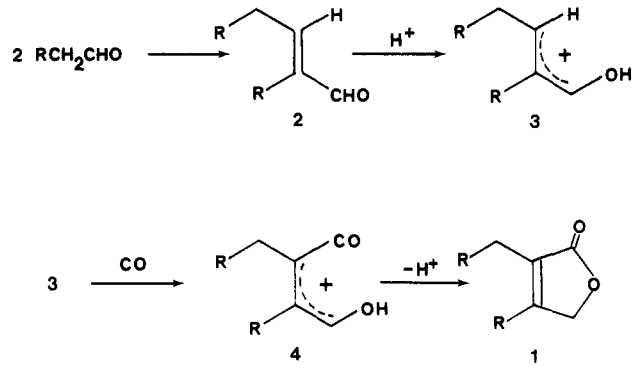


1 **2**

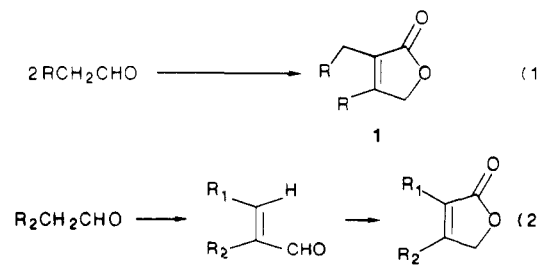
a: R_1 = H, R_2 = CH_3
b: R_1 = R_2 = CH_3
c: R_1 = R_2 = Et
d: R_1 = R_2 = *n*-pentyl

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

(1) Address correspondence to: The Dow Chemical Company, M. E. Pruitt Building, Midland, MI 48674.
(2) Bahrman, A. *New Synthesis with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: West Berlin, 1980; p 372.
(3) Koch, H.; Gilfert, W. *Brennst.-Chem.* **1955**, *30*, 321.
(4) Moller, K. E. *Brennst.-Chem.* **1966**, *47*, 10.
(5) Suzuki, S. U.S. Patent 3948977, 1976.
(6) Suzuki, S. U.S. Patent 3948986, 1976.
(7) The reported formation of 1-methyl-1,2-dicarboxycyclohexane (Himmele, W. Ger. Offen. 1277010, 1966) from cyclohexanecarboxaldehyde is not supported by structure proof.
(8) See: Woo, E. P.; Cheng, F. C. W. *J. Org. Chem.*, preceding paper in this issue.
(9) Neilsen, A. T.; Houlihan, W. J. *Org. React. (N.Y.)* **1976**, *16*.

0022-3263/86/1951-3706$01.50/0