Table II. Catalytic Carbonylation of Some Alkyl Chlorides by FeCRACO (RX/$FeCl_3$ = 10) at Atmospheric Pressure

1	reactn time, h	unreacted 1, %[b]	overall carbonylation, %[c]	2, %[d]	3, %[d]	4, %[d]	5, %[d]
1-chlorooctane	15	8	99	30	42	5	23
2-chlorooctane	60	8	34	35	65		
chlorocyclopentane	30	15	95	35	43	5	17
chlorocyclohexane	44	50	90	44	56		
chlorocyclooctane	14		48	48	31	21	

[a] Reactions performed at 65 °C in 50 mL of DME under carbon monoxide with the following reactant ratio: RX/NaH/Am-*t*-ONa/$FeCl_3$ = 10/40/20/1 mmol. [b] Determined by GLC analysis with internal standards. [d] Isolated yields based on consumed alkyl chloride. In all cases, the main side products were shown by GLC analysis to be reduction and elimination products of alkyl chlorides. [d] Relative percentages based on isolated yields.

This result strongly suggests that some monoelectronic transfer may occur, at least during the carbonylation of tertiary alkyl halides.[17]

Furthermore, unreported experiments indicated that, under the conditions used for CoCRACO[5], FeCRACO did carbonylate bromobenzene in DME to yield benzoic acid and *tert*-amyl benzoate. While the carbonylation yield was low (40%; the main reaction observed under these conditions was reduction to benzene), this reaction is the first example of carbonylation of C_6H_5Br by Na_2FeCO_4. Thus, it appears once again[4] that the complex reaction medium of MCRACO enables nucleophilic carbonyl metallates to participate in $S_{RN}1$ condensations with aryl halides.

We also examined the possibility of FeCRACO carbonylating primary and secondary alkyl halides using catalytic amounts of ferric salts. Results reported in Table II show that FeCRACO did effect such catalytic (RX/$FeCl_3$ = 10) carbonylations in good yields (up to 920% with respect to iron for a possible maximum of 1000%), indicating an easy regeneration of Na_2FeCO_4 during the reaction and thus allowing a good turnover of iron.

From this exploratory work, the following main conclusions may be drawn. First, the reaction of activated sodium hydride (NaH–Am-*t*-ONa) with $FeCl_3$ at 65 °C in DME under a slow stream of carbon monoxide leads to the formation of Na_2FeCO_4 under unusually mild conditions. Second, the multicomponent system in which it is formed allows reaction pathways other than SN_2 oxidative-addition,[13] as exemplified by the reaction of FeCRACO with tertiary alkyl halides and bromobenzene. It is tentatively suggested that, as CoCRACO, FeCRACO reacts with organic halides via an electron-initiated radical-chain mechanism of nucleophilic substitution.[18] Finally, FeCRACO allows catalytic carbonylation of primary and secondary alkyl halides.

Active work is being pursued in our laboratory to improve the yields and overall selectivity, to develop applications of FeCRACO in organic synthesis, and to elucidate the reaction mechanisms.

Experimental Section

The general carbonylation procedure is exemplified for 1-chlorooctane. The activated sodium hydride (NaH–Am-*t*-ONa, 40–20 mmol) was prepared (as previously described[5]) in 35 mL of DME under argon. After the mixture cooled to 0 °C, argon was replaced by a slow stream of carbon monoxide and $FeCl_3$ (10 mmol) was added (via a side arm) in small portions in order to avoid a too large temperature increase. Then the reaction medium was heated to 65 °C and stirred for 2 h under carbon monoxide. 1-Chlorooctane (10 mmol), in 5 mL DME, was then added together with the internal standard (the carbon monoxide stream was continued throughout the reaction). After 4 h at 65 °C, GLC analysis of a small aliquot indicated 2% unreacted chlorooctane. The reaction medium was cooled to 0 °C, poured on ice, and acidified with dilute HCl. Further classical workup and separations yielded nonanoic acid and, after column chromatography, nonanal, *tert*-amyl nonanoate, and its Claisen condensation product, identified by its spectroscopic properties and chemical degradation to 8-heptadecanone.

Acknowledgment. This work was supported by the Société Nationale Elf Aquitaine (Production) and by the Centre National de la Recherche Scientifique, France, which are gratefully acknowledged.

Registry No. $FeCl_3$, 7705-08-0; CO, 630-08-0; NaH, 7646-69-7; *t*-AmONa, 14593-46-5; 1-bromooctane, 111-83-1; 1-chlorooctane, 111-85-3; 2-bromooctane, 557-35-7; 2-chlorooctane, 628-61-5; bromocyclohexane, 108-85-0; chlorocylohexane, 542-18-7; 1-bromoadamantane, 768-90-1; 1-chloroadamantane, 935-56-8; 2-bromo-2-methyldodecane, 76402-83-0; 2-chloro-2-methyldodecane, 4325-53-5; chlorocyclopentane, 930-28-9; chlorocyclooctane, 1556-08-7; bromobenzene, 108-86-1.

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Electron-Transfer Processes. New Synthesis of γ-Lactones by Peroxydisulfate Oxidation of Aliphatic Carboxylic Acids in the Presence of Olefins

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Received December 19, 1980

The oxidation of organic compounds by peroxydisulfate in aqueous solution has been extensively studied,[1] while the oxidation in nonaqueous medium has received little attention.[2-5]

Recently, we reported the use of aliphatic carboxylic acids (i.e., acetic, propionic acids, etc.) as useful reaction media in the oxidation of aromatic hydrocarbons,[4] arylacetic acids, and aliphatic carboxylic acids[5] to give a variety of products, which are best explained as the result of electron transfer from the organic substrate to the $SO_4^{-\cdot}$ radical anion.[4,5]

In this note we describe a new synthesis of γ-lactones by peroxydisulfate oxidation of aliphatic carboxylic acids in the presence of olefins. From a synthetic point of view the method is an alternative to those based on the oxidation of the same acids by metal ions such as Mn(III),[6]

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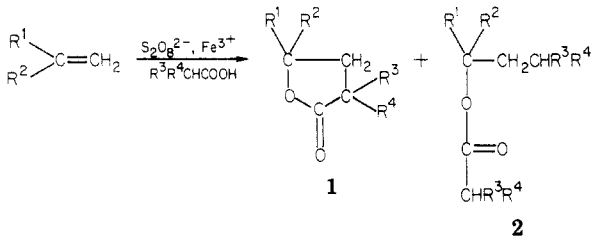
0022-3263/81/1946-3149$01.25/0

Table I. Preparation of γ-Lactones 1 and Esters 2

entry	products	R^1	R^2	R^3	R^4	temp, °C	olefin addn time, min	olefin conv, %	1, % yield	2, % yield
1	1a[6b] + 2a	C_6H_5	H	H	H	123	40	90	12	10
2	1a + 2a	C_6H_5	H	H	H	123	90	70	33	7
3	1a + 2a	C_6H_5	H	H	H	123	150	58	26	3
4	1b + 2b	4-Cl-C_6H_4	H	H	H	123	35	68	19	11
5	1b + 2b	4-Cl-C_6H_4	H	H	H	123	90	69	28	7
6	1c[6b]	n-C_6H_{13}	H	H	H	123	90	49	65	
7	1d[6b]	C_6H_5	CH_3	H	H	123	90	59	47	
8	1e	C_6H_5	CH_3	CH_3	H	136	90	38	78	
9	1f	C_6H_5	CH_3	CH_3	CH_3	142	90	12	70	

Ce(IV),[7] and Pb(IV),[8] with the advantage of using a more readily available and less expensive oxidant.

γ-Lactones (1) and, depending on the nature of the olefins, esters (2) were obtained when olefins were added slowly (in order to prevent direct oxidation by peroxydisulfate) at 120–145 °C to a heterogeneous mixture of potassium peroxydisulfate, a potassium aliphatic carboxylate, and a catalytic amount of basic ferric acetate in the corresponding aliphatic carboxylic acid. Reaction conditions and yields of 1 and 2, calculated on the basis of converted olefins, are reported in Table I.



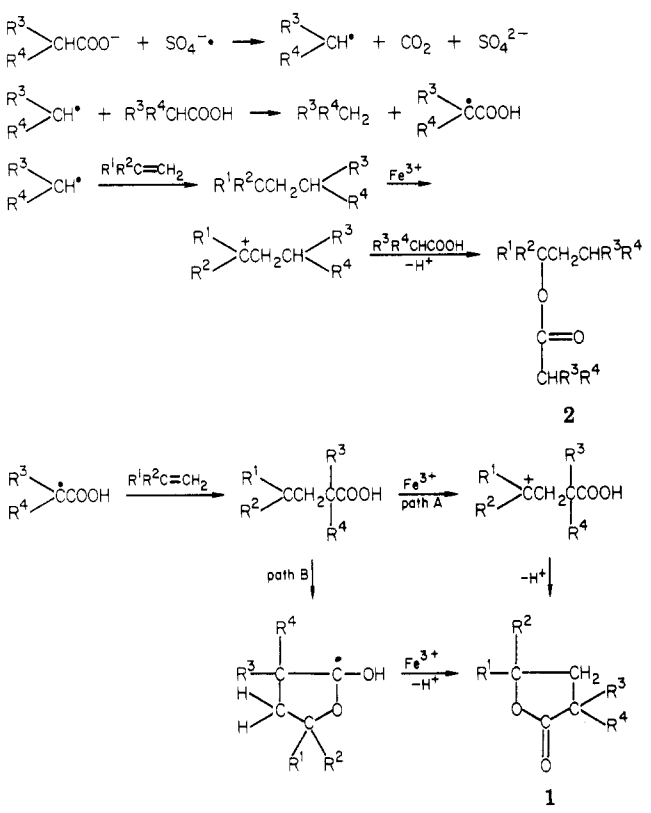
The formation of 1 and 2 is the result of the addition of carboxyalkyl and alkyl radicals to olefins according to the mechanism proposed in Scheme I. The following results evidence the presence of these two radical species in the acetic acid medium.

(i) Carbon dioxide and methane were observed during the reaction. When copper(II) acetate (a good oxidant for methyl radical[9]) was used instead of the Fe(III) salt, under similar conditions, lactone formation was completely prevented and methyl acetate was formed.

(ii) When the reaction was carried out in the presence of quinoxaline (a good trap of methyl radical[10]), olefin conversion and yields considerably decreased and a significant amount of methylquinoxaline was formed (see the Experimental Section).

Iron(III) is the metal of choice for this functionalization since it oxidizes secondary and tertiary benzyl radical intermediates at a faster rate than peroxydisulfate,[4] preventing extensive telomerization of styrenic olefins, and since it oxidizes alkyl radicals at a faster rate than the rate of hydrogen abstraction from an α C–H bond of a carboxylic acid by alkyl radicals. This latter observation and the known fast intramolecular addition of alkyl radicals to ketones, carboxylic acids, and esters[11] suggest that, with 1-octene, path B is more likely than path A (Scheme I). Moreover, the Fe(II) salt, produced during the reaction, catalyzes the peroxydisulfate decomposition.

Scheme I



Experimental Section

Potassium peroxydisulfate and basic ferric acetate were purchased from Fluka; the other reagents also are commercially available. The data reported in Table I were obtained according to the procedure given below for the preparation of **1d**. Yields are based on the converted olefins. In the preparation of **1e**, propionic acid and potassium propionate were used instead of acetic acid and potassium acetate, respectively. Analogously, in preparation of **1f**, isobutyric acid and potassium isobutyrate were used. The compounds listed in Table I were isolated as pure. Known products were identified by comparison with authentic samples: 2-methylquinoxaline (bp 245–247 °C), 2,3-dimethylquinoxaline (mp 104–106 °C), 5-*n*-hexyl-4,5-dihydro-2(3*H*)-

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furanone **1c** [bp 142–143 °C (8 mmHg)] and 5-phenyl-4,5-dihydro-2(3*H*)-furanone **1a** (mp 36–37 °C) were obtained from Aldrich; 1-phenyl-1-propyl acetate **2a** [bp 105 °C (16 mmHg)] and 1-(4-chlorophenyl)-1-propyl acetate **2b** [bp 135–137 °C (18 mmHg)] were prepared according to a known procedure;[12] 5-(4-chlorophenyl)-4,5-dihydro-2(3*H*)-furanone **1b**; (mp 43–44 °C) was prepared by the known method.[13] The lactones **1d–f** were identified on the basis of their IR (Perkin-Elmer E-177), ^1H or ^{13}C NMR (Varian A 90 or A 100 instrument), mass spectral data (GLC–MS system Varian MAT 112 S), and elemental analyses (C, ±0.2%; H, ±0.2%). All lactones isolated present an IR carbonyl stretching between 1775 and 1790 cm^{-1}.

Synthesis of 5-Phenyl-5-methyl-4,5-dihydro-2(3*H*)-furanone (1d). A solution of α-methylstyrene (0.02 mol) in acetic acid (7.5 mL) was added dropwise during 90 min to a well-stirred mixture of potassium peroxydisulfate (0.01 mol), potassium acetate (0.16 mol), and basic ferric acetate (0.005 mol) in acetic acid (42.5 mL) kept at 123 °C. The reaction mixture was stirred for an additional 30 min at 123 °C. Peroxydisulfate was found to be completely decomposed by iodometric titration of the insoluble inorganic salt after cooling, filtering, and washing with acetic acid. Carbon dioxide (0.41 g, 0.0093 mol) and methane (0.0091 g, 0.005 mol) were determined by trapping on KOH pellets and by GLC (molecular sieves (3 Å), 1 m, 100 °C), respectively. The reaction mixture was cooled, diluted with water, and extracted with ether. The organic extracts were combined and washed with 0.2 N HCl (100 mL) and with a saturated Na_2CO_3 solution (4 × 100 mL). The organic solution, after addition of methylbenzoate as internal standard, was analyzed by GLC on a column (2 m) of 10% UCC W 982 on Chromosorb W (80–100 mesh) with a Hewlett-Packard Model 575. The conversion of α-methylstyrene was 59% to give **1d** (47% yield, based on converted α-methylstyrene).

In a parallel experiment, on 10 times scale, the crude reaction product was chromatographed on silica gel (70–230 mesh), using an *n*-pentane–ether (80:20) mixture as eluent. **1d** (9.4 g, 0.053 mol, 45% yield) was isolated as an oil; an analytically pure sample was obtained by distillation in vacuo: bp 116–117 °C (1.8 mmHg) [lit.[14] bp 104–106 °C (0.1 mmHg)]; ^1H NMR ($CDCl_3$) δ 1.70 (s, 3 H), 2.47 (m, 4 H), 7.25 (m, 5 H); mass spectrum, *m/e* 161 (100), 43 (81), 105 (49), 121 (47), 77 (34), 51 (26), 56 (25), 176 ($M^{+\cdot}$, 7).

In a parallel experiment, carried out in the presence of $Cu(OAc)_2 \cdot H_2O$ (0.25 g, 0.00125 mol), **1d** was present only in a trace amount.

Synthesis of 5-Phenyl-3,5-dimethyl-4,5-dihydro-2(3*H*)-furanone (1e). The reaction was carried out as indicated in Table I. The **1e** was isolated by column chromatography on silica gel (pentane–ether eluent) and found to be a mixture of two diastereoisomers in the ratio 1:1; each diastereoisomer was isolated as pure during chromatography.

First diastereoisomer (to be eluted): bp 101–102 °C (1.4 mmHg); ^1H NMR ($CDCl_3$) δ 1.25 (d, 3 H, J = 7.5 Hz), 1.74 (s, 3 H), 2–3 (m, 3 H), 7.25 (m, 5 H); ^{13}C NMR ($CDCl_3$) 84.59 (C5), 45.06 (C4), 35.11 (C3), 179.32 (C2), 30.36 (CH_3-C5), 14.82 (CH_3-C3); mass spectrum, *m/e* 105 (100), 174 (54), 43 (66), 77 (37), 42 (35), 131 (23), 121 (10), 190 ($M^{+\cdot}$, 3).

Second diastereoisomer (to be eluted): bp 104–106 °C (1.4 mmHg); ^1H NMR ($CDCl_3$) δ 1.25 (d, 3 H, J = 7.5 Hz), 1.67 (s, 3 H), 2–3.2 (m, 3 H), 7.3 (m, 5 H); ^{13}C NMR ($CDCl_3$) 84.58 (C5), 44.14 (C4), 35.37 (C3), 178.99 (C2), 28.86 (CH_3-C5), 15.54 (CH_3-C3); mass spectrum, *m/e* 105 (100), 175 (54), 43 (66), 77 (37), 42 (35), 131 (23), 121 (18), 190 ($M^{+\cdot}$, 3).

Synthesis of 5-Phenyl-3,3,5-trimethyl-4,5-dihydro-2-(3*H*)-furanone (1f). Prepared as described in Table I, the lactone **1f** was isolated pure by column chromatography on silica gel (pentane–ether (9:1) eluent): bp 111–112 °C (1.5 mmHg); ^1H NMR ($CDCl_3$) δ 1.00 (s, 3 H), 1.35 (s, 3 H), 1.72 (s, 3 H), 2.2–2.7 (AB q, 1 H + 1 H, J = 14.25 Hz), 7.3 (m, 5 H); ^{13}C NMR ($CDCl_3$) 83.54 (C5), 50.84 (C4), 40.96 (C3), 181.92 (C2), 26.85 (CH_3-C3), 26.07 (CH_3-C3), 32.12 (CH_3-C5); mass spectrum, *m/e* 105 (100), 43 (54), 189 (32), 145 (29), 77 (27), 56 (21), 121 (19), 204 ($M^{+\cdot}$, 3).

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Oxidation of Acetic Acid in the Presence of Styrene and Quinoxaline. A solution of styrene (0.02 mol) in acetic acid (7.5 mL) was added dropwise during 90 min to a stirred mixture of $K_2S_2O_8$ (0.01 mol), KOAc (0.16 mol), basic ferric acetate (0.005 mol), and quinoxaline (0.02 mol) in acetic acid (42.5 mL) at 123 °C. The reaction mixture was stirred for an additional 30 min at 123 °C. CO_2 (0.27 g, 0.0055 mol) and methane (0.021 g, 0.0012 mol) were determined. The reaction mixture was cooled, diluted with water, and extracted with ether as in the preparation of **1d**. From GLC data, the conversion of styrene was 36% to give **1a** (15% yield based on converted styrene) and **1b** (5% yield based on converted styrene). The conversion of quinoxaline was 26% to give 2-methylquinoxaline (57% yield based on converted quinoxaline) and dimethylquinoxaline (4% yield).

Acknowledgment. We thank Professor F. Minisci for stimulating discussions and Mr. G. Calcaterra for skillful technical assistance.

Registry No. **1a**, 1008-76-0; **1b**, 18410-18-9; **1c**, 706-14-9; **1d**, 21303-80-0; **1e** (isomer 1), 77415-37-3; **1e** (isomer 2), 77415-38-4; **1f**, 77415-39-5; **2a**, 2114-29-6; **2b**, 77415-40-8; propionic acid, 79-09-4; isobutyric acid, 79-31-2; α-methylstyrene, 98-83-9; potassium peroxydisulfate, 7727-21-1; acetic acid, 64-19-7; styrene, 100-42-5; quinoxaline, 91-19-0; 2-methylquinoxaline, 7251-61-8; 2,3-dimethylquinoxaline, 2379-55-7.

A Facile One-Step Synthesis of Diethyl [2-^{13}C]Malonate from Ethyl [2-^{13}C]Acetate

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Received March 20, 1981

Malonic acid and its esters, labeled with ^{13}C or ^{14}C at C-1 or C-2, have been used extensively in biosynthetic studies and as intermediates for the synthesis of more complex labeled compounds.[2] Malonic acid and its diethyl ester have usually been made from acetic acid, via bromo- or chloroacetic acid and cyanoacetate.[4] A 71% yield of diethyl [1-^{13}C]malonate was obtained from [1-^{13}C]acetic acid;[4b] however, the ^{13}C content of the product (40%) was less than that in the acetic acid (52%). This loss was attributed to exchange of the enriched acetic acid with unlabeled acetic anhydride used in the Hell–Volhard–Zellinsky bromination of acetic acid.

Rathke[5] obtained the lithium enolate of ethyl acetate by reaction of lithium bis(trimethylsilyl)amide with ethyl acetate in tetrahydrofuran at −78 °C. This salt is stable at low temperatures and reaction with aldehydes and ketones affords excellent yields of β-hydroxy esters.[5,6] We considered that diethyl malonate could be formed in one

(1) Contribution No. 177 from this laboratory.
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0022-3263/81/1946-3151$01.25/0