J. Org. Chem. 1981, *46*, 3147–3149 **3147**

Calcd for $C_{14}H_{28}O_3Si$: C, 61.72; H, 10.36. Found: C, 61.79; H, 10.45.

(1*S,5*R*,9*R*)-9-[(*tert*-Butyldimethylsilyl)oxy]-3-oxo-2,4-dioxa-3-thiatricyclo[5.3.1.$0^{5,10}$]undecane (7).** A solution of *N,N'*-thionyldiimidazole was prepared by dissolving 899 mg (13.2 mmol) of imidazole in 20 mL of THF, cooling to 2 °C, and adding 238 mL (3.31 mmol) of thionyl chhloride. The resulting suspension was added dropwise via cannula through a glass filter frit to a cold (−15 °C), stirred solution of 300 mg (1.10 mmol) of diol **6**. The cooling bath was removed and the reaction mixture stirred for 1 h. After evaporation of ca. 75% of the solvent, the clear, residual oil was chromatographed on 35 g of silica gel with Et_2O–hexane (1/2), affording 331 mg (94%) of the mixture of sulfurous esters **7** as a clear colorless oil: ^1H NMR (360 MHz) δ 4.90–4.83 (m, 1 H), 4.54–4.48 (m, 1 H), 3.98–3.89 (m, 1 H), 3.57 (q, $J = 4$ Hz, 0.6 H), 2.76–2.67 (d, $J = 16$ Hz, 1.2 H), 2.51 (q, $J = 4$ Hz, 0.4 H), 2.19–2.08 (m, 1 H), 2.00–1.70 (methylene envelope, 4 H), 1.31–1.22 (m, 1 H); ^1H NMR (100 MHz) δ 5.04–4.81 (m, 1 H), 4.68–4.46 (m, 1 H), 4.10–3.86 (m, 1 H), 3.60 (q, $J = 4$ Hz, 0.6 H), 2.82 (q, 0.4 H), 2.67 (q, 0.4 H), 2.52 (q, $J = 4$ Hz, 0.4 H), 2.34–1.10 (methylene envelope, 6.2 H), 0.86 (s, 9 H), 0.03 (s, 6 H); IR ($CHCl_3$) 2955, 1185, 1101 cm^{-1}; mass spectrum, *m/e* 318 (M^+, 1), 261 (10), 197 (84), 153 (26), 79 (70), 77 (100), 59 (27), 41 (25).

(1*S,5*R*,9*R*)-9-[(*tert*-Butyldimethylsilyl)oxy]-3,3-dioxo-2,4-dioxa-3-thiatricyclo[5.3.1.$0^{5,10}$]undecane (8).** To a solution of 445 mg (1.40 mmol) of **7** in 10 mL of CCl_4 was added 35.8 mL (1.68 mmol) of a 0.048 M solution of RuO_4 in CCl_4. The black RuO_2 precipitate was filtered off and washed twice with 5-mL portions of CCl_4 and the filtrate concentrated to a yellow oil which crystallized in vacuo (400 mg). Recrystallization from 5 mL of hexane afforded 334 mg (72%) of sulfate **8** as white plates: mp 79.5–80.5 °C; ^1H NMR (100 MHz) δ 5.38–5.12 (m, 1 H), 5.02–4.78 (m, 1 H), 4.18–3.97 (dt, $J_t = 9$, $J_d = 4$ Hz, 1 H), 3.08 (q, $J = 4$ Hz, 1 H), 2.56–1.63 (methylene envelope, 6 H), 1.42–1.16 (dq, $J_d = 15$ Hz, 1 H), 0.83 (s, 9 H), 0.04 (s, 6 H); IR ($CHCl_3$) 2955, 1383, 1195, 990, 977 cm^{-1}; mass spectrum, *m/e* 334 (M^+, 1), 277 (100), 197 (37), 79 (45), 75 (97). Anal. Calcd for $C_{14}H_{26}O_5SSi$: C, 50.27; H, 7.83; S, 9.59. Found: C, 50.29; H, 7.69; S, 9.68.

(1*S,5*R*,9*R*)-3,3-Dioxo-2,4-dioxa-3-thiatricyclo[5.3.1.$0^{5,10}$]undecan-1-ol (1).** Hydrogen fluoride is an extremely dangerous reagent. All reactions using this substance must be done in a well-ventilated hood, taking the utmost precautions against inhalation of or contact with the vapor.[20]

In a Teflon test tube (2 × 15 cm) fitted with Teflon stopper and Teflon inlet and outlet tubes was placed 259 mg (0.772 mmol) of **8**. The test tube was then cooled in a dry ice–*i*-PrOH bath and ca. 5 mL of HF was condensed in the tube. The vessel was swirled gently and then transferred to a −20 °C bath (dry ice–*i*-PrOH), and a stream of argon was passed over the surface to remove the HF (ca. 1.5 h). The yellow residue was partitioned between H_2O and CH_2Cl_2 (2 mL each). The aqueous layer was separated and extracted with three 5-mL portions of CH_2Cl_2. The combined CH_2Cl_2 extracts were dried ($MgSO_4$) and evaporated to give an off-white oil which crystallized in vacuo (166 mg). Recrystallization from CH_2Cl_2 (2 mL)–hexane (5 mL) afforded 150 mg (88%) of **1** as off-white crystals: mp 109–110 °C dec; ^1H NMR (100 MHz) δ 5.42–5.19 (m, 1 H), 5.07–4.86 (m, 1 H), 4.37–4.08 (m, 1 H), 3.20 (q, $J = 4$ Hz 1 H), 2.56–1.60 (methylene envelope, 7 H), 1.45–1.18 (dm, $J_d = 15$ Hz, 1 H); IR ($CHCl_3$) 3610, 2950, 1383, 1193, 984, 955 cm^{-1}; mass spectrum, *m/e* no M^+, 122 (27), 96 (25), 95 (39), 79 (56), 78 (100), 77 (25), 41 (29), 40 (25). Anal. Calcd for $C_8H_{12}O_5S$: C, 43.62; H, 5.49; S, 14.56. Found: C, 43.77; H, 5.44; S, 14.45.

3,3,6,6,9-Pentamethyl-2-azonia-10-azabicyclo[4.4.0]dec-1-ene 6,7-oxybicyclo[2.2.2]oct-2-yl Sulfate (2). To a solution of 50 mg (0.227 mmol) of **1** in 500 μL of DMF in a small test tube (7 × 60 mm) fitted with a rubber septum under Ar was added 103 μL (0.45 mmol, $d^{20}{}_4$ 0.918) of **9**. A white, crystalline precipitate slowly formed overnight. After 9 days TLC analysis of the supernatant liquid indicated complete consumption of the educt. The mixture was diluted with 200 μL of Et_2O and 500 μL of hexane. The crystals were collected by filtration and dried in vacuo (50 mg). Recrystallization from CH_2Cl_2–Et_2O followed by drying at 40 °C in vacuo gave 44.5 mg (46%) of **2** as white, fluffy needles: mp 208–209 °C; ^1H NMR (100 MHz) δ 9.10–8.80 (s, 2 H), 4.70–4.45 (m, 3 H), 3.91–3.70 (m, 1 H), 2.40–1.20 (methylene envelope, 15 H), 1.36 and 1.30 (2 s, 15 H); ^{13}C NMR (25 MHz) δ 167.52 (s), 80.31 (d), 79.88 (d), 69.20 (d), 54.44 (s), 39.44 (d), 37.81 (t), 34.32 (t), 34.08 (t), 32.08 (s), 31.03 (2 t), 30.92 (2 t), 30.70 (2 q), 29.84 (2 q), 25.23 (d), 24.61 (q); IR ($CHCl_3$) 3220, 3110, 3005, 2975, 2950, 1642, 1255, 1242, 1021, 950 cm^{-1}; mass spectrum, *m/e* 427 ($M^+ - 1$,1) 193 (100), 180 (37), 165 (27), 84 (26), 81 (52), 69 (84), 57 (36), 55 (34), 45 (44), 44 (59), 43 (39), 41 (47). Anal. Calcd for $C_{21}H_{36}N_2O_5S$: C, 58.85; H, 8.47; N, 6.54; S, 7.48. Found= C, 58.77; H, 8.52; N, 6.41; S, 7.52.

Acknowledgment. I thank Professor Dr. Albert Eschenmoser for suggesting this problem to me, for his generous financial support, and for many stimulating discussions.

Registry No. 1, 77773-84-3; **2**, 77773-86-5; **3**, 36520-55-5; **4**, 77773-87-6; **5**, 77773-88-7; **6**, 77773-89-8; **7**, 77773-90-1; **8**, 77773-91-2; **9**, 69340-58-5.

---

[20] I thank Professor R. Gut, Department of Inorganic Chemistry, ETH, for his assistance with this problem and for performing the experiment.

Activation of Reducing Agents. Sodium Hydride Containing Complex Reducing Agents. 16.[1] FeCRACO, a New Reagent for Carbonylation of Primary, Secondary, and Tertiary Alkyl Halides at Atmospheric Pressure

Jean-Jacques Brunet, Christian Sidot, and Paul Caubere*

Laboratoire de Chimie Organique I, ERA CNRS No. 476,
Université de Nancy I, Case Officielle 140, 54037 Nancy,
Cédex, France

Received January 6, 1981

In recent years, complex reducing agents "NaH–RONa–MX_n"[2] (termed CRA and MCRA when the nature of the metallic salt must be specified) have been described as versatile, inexpensive reagents in organic synthesis and useful applications have already been devised.[3] In particular, it seemed that CRA, prepared under carbon monoxide, could be used for the generation of transition-metal carbonyl species under very mild conditions in an aprotic medium. Thus, it has been found that "NaH–Am-*t*-ONa–$Co(OAc)_2$–CO" led to the generation (room temperature, 1 atm) of $NaCoCO_4$ in a multicomponent medium,[4] termed CoCRACO. Furthermore it has been evidenced that the simultaneous presence of NaH and Am-*t*-ONa promotes $S_{RN}1$ condensations of $NaCoCO_4$ with aryl halides,[4] thus allowing catalytic carbonylation of aryl halides[5] under unusually mild conditions for cobalt carbonyl species.

On the other hand, we have also briefly reported[6] that "NaH–Am-*t*-ONa–$FeCl_3$–CO" led to iron carbonyl species

---

[1] Part 15: R. Vanderesse, J. J. Brunet, and P. Caubere, *J. Org. Chem.*, **46**, 1270 (1981).

[2] J. J. Brunet, R. Vanderesse, and P. Caubere, *J. Organomet. Chem.*, **157**, 125 (1978).

[3] J. J. Brunet, P. Gallois, and P. Caubere, *J. Org. Chem.*, **45**, 1937 (1980); P. Gallois, J. J. Brunet, and P. Caubere, *ibid.*, **45**, 1946 (1980); L. Mordenti, J. J. Brunet, and P. Caubere, *ibid.*, **44**, 2203 (1979); J. J. Brunet, L. Mordenti, and P. Caubere, *ibid.*, **43**, 4804 (1978); J. J. Brunet, L. Mordenti, B. Loubinoux, and P. Caubere, *Tetrahedron Lett.* 1069 (1977); J. J. Brunet and P. Caubere, *ibid.*, 3947 (1977).

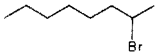
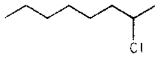
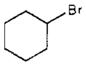
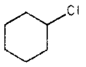
[4] J. J. Brunet, C. Sidot, and P. Caubere, *J. Organomet. Chem.*, **204**, 229 (1980).

[5] J. J. Brunet, C. Sidot, B. Loubinoux, and P. Caubere, *J. Org. Chem.*, **44**, 2199 (1979).

[6] B. Loubinoux, B. Fixari, J. J. Brunet, and P. Caubere, *J. Organomet. Chem.*, **105**, C22 (1976).

0022-3263/81/1946-3147$01.25/0

Table I. Carbonylation of Alkyl Halides by FeCRACO[a] ($RX/FeCl_3 = 1$) at Atmospheric Pressure

1	reacn temp, °C	reactn time, h	unreacted 1, %[b]	overall carbonylation, %[c]	2, %[d]	3, %[d]	4, %[d]	5, %[d]
$C_8H_{17}Br$	20	20	20	75	24	43	33	
$C_8H_{17}Cl$	65-70	4	2	96	18	40	16	26
	20	53	5	68	15	47	38	
	65-70	13	12	60	37	53	10	
	30	40	10	70	44	56		
	65-70	36	20	75	33	67		
1-bromoadamantane	40	84	18	88	22	78		
1-chloroadamantane	65-70	80	65	80	43	57		
$C_{10}H_{21}C(Br)Me_2$	65	80	75	20	99	trace		
$C_{10}H_{21}C(Cl)Me_2$	65-70	48	46	32	60	40		

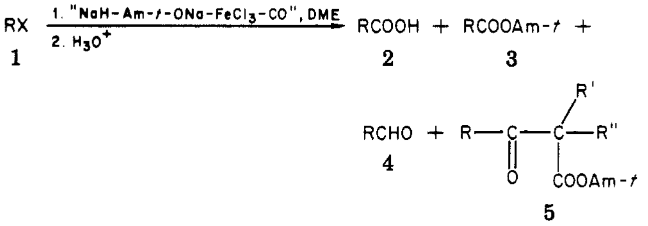
[a] Reactions performed in 50 mL of DME under CO with the following reactant ratio: RX/NaH/Am-*t*-ONa/$FeCl_3$ = 10/40/20/10 mmol. [b] Determined by GLC analysis with internal standards. [c] Isolated yields, based on consumed alkyl halide. In all cases, the side products were shown by GLC to be the corresponding alkanes and alkenes. [d] Relative percentages based on isolated yields.

(termed FeCRACO). It might be expected that FeCRACO could be constituted of Na_2FeCO_4 or $NaHFeCO_4$. Recording the IR spectrum[7] of the soluble part of "NaH–Am-*t*-ONa–$FeCl_3$–CO", prepared in 1,2-dimethoxyethane (DME) (vide infra), led to the following observations: the IR spectrum is constituted of two very weak bands near 1915 and 1870 cm^{-1} (attributed to some minute amounts of $Na_2Fe_2CO_8$)[8] and a broad band centered at 1775 cm^{-1} with shoulders at 1790 and 1755 cm^{-1}. In spite of some inconsistancies in the literature about the IR spectrum of Na_2FeCO_4,[9-12] it seemed that the main bands we observed at 1775 cm^{-1} might be attributed to Na_2FeCO_4. To verify this attribution, pure Na_2FeCO_4 was prepared in THF by Collman's procedure.[13] The solid reagent thus obtained was dissolved in DME.[14] The IR spectrum of this solution exhibited the same absorptions as FeCRACO in the 1795–1755-cm^{-1} region.

Thus it appeared that, concerning the carbonyl species, FeCRACO is mainly constituted of Na_2FeCO_4. While the conversion of $FeCl_3$ to Na_2FeCO_4 (as the conversion of $Co(OAc)_2$ to $NaCoCO_4$) appeared far from quantitative, the formation of this carbonyl dianion from ferric salt under such mild conditions (vide infra) is unprecedented.[15]

The reactivity of the supernucleophile[13] Na_2FeCO_4 is well documented.[16] However, it could be conjectured that, as for $NaCoCO_4$ in CoCRACO,[4,5] the reactivity of Na_2FeCO_4 in FeCRACO should be different from that of pure Na_2FeCO_4. Thus, it was decided to investigate the reactivity of FeCRACO, and we report here our first results with organic halides.

Scheme I



Reaction with alkyl halides appeared well suited for comparison of the reactivity of FeCRACO with that of Na_2FeCO_4.[13] Under the experimental conditions defined below, FeCRACO reacted with alkyl halides (see Scheme I) to yield a mixture of the corresponding acid, aldehyde, ester, and, in a few cases, the β-keto ester arising from "in situ" Claisen condensation. The main results are reported in Table I.

As may be seen from Table I, FeCRACO promoted carbonylation of primary, secondary, and, interestingly, tertiary alkyl halides. With the two first classes of halides, rather good overall carbonylation yields were obtained. Tertiary alkyl halides, such as 1-bromoadamantane, were slowly carbonylated. Although more drastic conditions were used for tertiary alkyl halides, it is noteworthy that, as for primary and secondary halides, reduction and elimination side reactions were not very significant.

Thus, while the conversion of tertiary alkyl halides was low, the reactivity of FeCRACO appeared in sharp contrast to that of Na_2FeCO_4 which has been reported to give no observable reaction with 1-bromoadamantane in 9 days.[13]

---

(7) IR spectra were recorded on a Perkin-Elmer spectrophotometer, Model 580 B. A standard 0.05-mm cavity cell and a variable-path cell (micrometer type), with NaCl windows, were used.

(8) W. F. Edgell, M. T. Yang, B. J. Bulkin, and N. Koizumi, *J. Am. Chem. Soc.*, **87**, 3080 (1965).

(9) IR spectra of Na_2FeCO_4 have been reported in aqueous solution[10] (1786 cm^{-1}), in Nujol[11] (1761 cm^{-1}), and in DMF solution[8] (1730 cm^{-1}). However, it is well established[12] that DMF cannot be used in the 1780–1700 cm^{-1} region!

(10) W. F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell, and G. Asato, *J. Am. Chem. Soc.*, **82**, 1254 (1960).

(11) K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 2239 (1969).

(12) See, for example, M. Avram and G. H. D. Matescu, "La Spectroscopie Infrarouge", Dunod, Paris, 1970.

(13) J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 2515 (1977).

(14) An identical IR spectrum was obtained by reduction of $Fe(CO)_5$ with benzophenone ketyl in DME.

(15) See, for example, "Organic Syntheses via Metal Carbonyls", Vols. 1 and 2, I. Wender and P. Pino, Eds, Wiley-Interscience, New York, 1968 and 1977.

(16) J. P. Collman, *Acc. Chem. Res.*, **8**, 342 (1965), and references cited therein; J. E. Ellis, *J. Organomet. Chem.*, **86**, 1 (1975); J. P. Collman, R. K. Rothrock, R. G. Finke, and F. R. Munch, *J. Am. Chem. Soc.*, **99**, 7381 (1977); G. L. Geoffroy and W. L. Gladfelter, *ibid.*, **99**, 7565 (1977); Y. Watanabe, T. Mitsudo, M. Tanaka, K. Yamamoto, T. Okajima, and Y. Takegami, *Bull. Chem. Soc. Jpn.*, **44**, 2569 (1971); Y. Watanabe, M. Yamashita, T. Mitsudo, M. Igami, and Y. Takegami, *ibid.*, **48**, 2490 (1975).

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 S_N2 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 Sociêtê 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.

---

(17) See, for example, J. K. Kochi "Organometallic Mechanisms and Catalysts", Academic Press, New York, 1978, and references cited therein.

(18) J. F. Bunnett, *Acc. Chem. Res.*, 11, 413 (1978). See also: G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.*, **90**, 347 (1968); N. Kornblum, R. E. Michel, and R. C. Kerber, *ibid.*, **88**, 5560 and 5662 (1966); G. A. Russell and W. C. Danen, *ibid.*, 88 5663 (1966); R. C. Kerber, G. W. Urry, and N. Kornblum, *ibid.*, **86**, 3904 (1964); *ibid.*, **87**, 4520 (1965).

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

Claudio Giordano,*† Aldo Belli,† Francesco Casagrande, and Gianfranco Guglielmetti

Istituto Ricerche G. Donegani S.p.A., 28100 Novara, Italy

Attilio Citterio*

Istituto di Chimica del Politecnico, 20133 Milano, Italy

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]

---

† Present address: Blasinachim S.p.A., 20100 Milano, Italy.