20. Nucleophilic 1,2-Shifts of Alkoxycarbonyl and Carboxylate Groups in the Benzilic-Acid Type Rearrangement of α,β-Dioxobutyric Esters[1])

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tert-Butyl α,β-dioxobutyrate (hydrate; **1d**) undergoes, at medium or high pH, the benzilic-acid rearrangement with exclusive 1,2-shift of the COO(*t*-Bu) group; the same is true for the corresponding isopropyl ester **1c** and ethyl ester **1b** at high pH, whereas at lower pH, the overall picture of these reactions is complicated by concurrent hydrolysis of the ester, followed by a 1,2-shift of the COO^- group. Consequently, the shift of these electron-attracting groups cannot be considered to be systematically disfavoured (compared, *e.g.*, with alkyl-group shifts). Kinetic measurements of the rearrangement show for both esters (as well as for the analogous ethyl ester **1b**, and also for ethyl 3-cyclopropyl-α,β-dioxopropionate (**4**)) a characteristic rate profile: at relatively low pH, k is proportional to $[HO^-]$, approaching saturation with increasing $[HO^-]$ (interpreted as complete transformation of the substrate into the hydrate monoanion), which is followed at higher pH by another rate increase with k proportional to $[HO^-]$ (probably due to the reaction of the hydrate dianion). The similarity of k values for **1b–d** shows that in the shift of COOR steric hindrance caused by R is negligible.

1,2-Shifts of electron-withdrawing groups towards electron-deficient centres might be considered to be disfavoured. They have, however, been demonstrated in a significant number of cases, comprising *Wagner-Meerwein*, pinacol, and benzilic-acid rearrangements [2]. The course of these shifts depends upon factors more important than electron abundance in the migrating group, factors which have to be established individually for each reaction type.

In the case of the benzilic-acid rearrangement, we have shown [3] that the action of alkali on (hydrated) ethyl α,β-dioxobutyrate (**1b**) [4] comprises two different reactions (*Scheme 1*): *A*) a direct 1,2-shift of the unhydrolyzed COOEt group takes place at higher pH ($\geq$ 14), with subsequent hydrolysis of the ester group (**3b**→**2**); *B*) at lower pH ($<$ 10), the ester group is hydrolyzed first and a COO^- group is shifted. The first reaction corresponds to preferential attack of HO^- on the geminal-diol group at C(2) (keto hydrate), the second to preceding attack of HO^- on the ester carbonyl group of **1**. Both reaction paths yield methyltartronate **2**[3]). Correspondingly, (hydrated) *tert*-butyl α,β-dioxobutyrate (**1d**) which cannot be hydrolyzed by alkali shows only ester-group migration upon treatment with NaOH forming *tert*-butyl 2-methyltartronate (**3d**) [6]. As a result one can state that, in principle, carboxylate as well as ester groups can migrate in the benzilic-acid rearrangement.

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[1]) Reductones and Tricarbonyl Compounds, Part 31. Part 30: [1].

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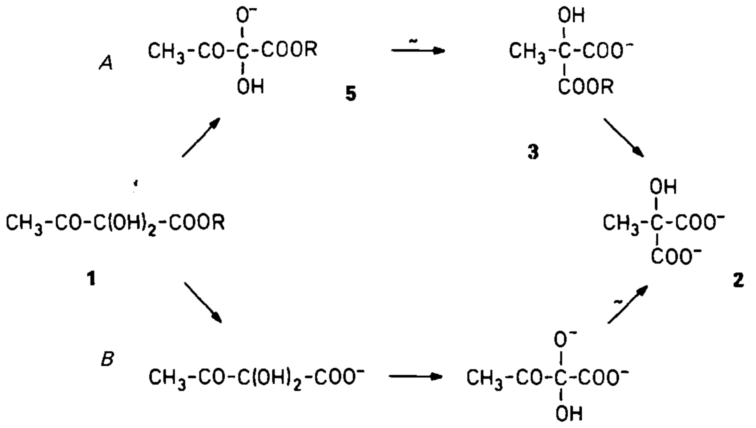
[3]) A third reaction path is open to α,β-dioxopropionates substituted at the β-position by electron-attracting groups, *e.g.* aryl or CF_3: *via* an attack of HO^- on the β-carbonyl group, a *retro*-aldol-type cleavage takes place [5]: $Ar{-}CO{-}C(OH)_2{-}COOR \rightarrow Ar{-}COO^- + HC(OH)_2{-}COOR$.

Scheme 1



a R = H
b R = Et
c R = i-Pr
d R = *t*-Bu

In order to better understand the ratio of carboxylate- to ester-group migration, *i.e.* the ratio of attack of HO^- on the ester-carbonyl and the geminal-diol groups, including the equilibria involved, we have examined the rearrangement and hydrolysis of (hydrated) isopropyl α,β-dioxobutyrate (**1c**) and have measured the rates of reaction of the isopropyl and *tert*-butyl esters **1c** and **1d**, respectively, to compare them with that of the ethyl ester **1b** [3].

Isopropyl α,β-dioxobutyrate (**1c**) was prepared from isopropyl acetoacetate by oxidation of its oximino derivative with N_2O_4, following a procedure elaborated for **1b** [7]. Ester **1d** had been prepared previously [6].

The ethyl ester crystallizes as a (cyclic) dimer hemihydrate [7]. NMR data had shown that it exists in this form in aprotic solutions, whereas in aqueous solution it is rapidly transformed into an equilibrium mixture containing the monomer monohydrate **1b** and dimer hemihydrate forms. The *tert*-butyl ester **1d**, on the other hand, exists as the (monomer) monohydrate **1d** [6]. The isopropyl ester takes an intermediate position: the crystals contain 0.5 mol of H_2O, and a freshly prepared solution in D_2O shows H-NMR signals of the methyl groups of CH_3CO and of $CH_3C(OH)O$– belonging to a (presumably cyclic) hemiacetal form; upon aging, the latter disappears, probably by transformation into the monohydrate form **1c**; the UV absorption of the yellow unhydrated form is absent from the aqueous solutions.

Upon treatment with aqueous alkali, **1c** is transformed into the dianion **2** of methyltartronic acid; at pH ≈ 9, the transformation takes several days, at pH ≈ 14, it is complete in 1 h[4]).

For the ethyl ester **1b** it had been shown [3] [4] by ^{14}C-labelling that the rearrangement takes place *via* the shift of the COOEt (at high pH) or COO^- group (at lower

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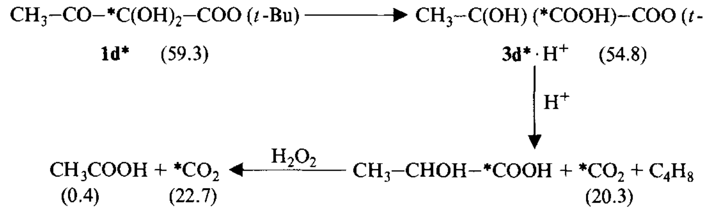
[4]) When **1b–d** had not been carefully purified by distillation followed by recrystallization of the hydrates, they showed no rearrangement but only *retro*-aldol cleavage to CH_3COOH and OCH–COOR[3]). This side reaction seems to be catalyzed by N-containing impurities introduced by the preparation procedure. Indeed, purified hydrate **1b** showed cleavage instead of rearrangement when small amounts of hydrazine or hydroxylamine were added to the solution, particularly at lower pH where the rearrangement is slow.

Scheme 2. *Degradation of the ^{14}C-Labelled* **3d***. In parentheses: specific activity in nCi/mmol.



pH), excluding the migration of the CH_3 group to the central (hydrated) carbonyl group. For the *tert*-butyl ester **1d**, migration of COO(*t*-Bu) had analogously been demonstrated for the higher pH range [6]. In order to make sure that the mechanism does not change with pH, we repeated the rearrangement at lower pH with **1d*** labelled with ^{14}C in C(2) (see *Scheme 2*). The stepwise degradation of the product **3d***·H$^+$ showed that it contained the label only in the carboxylic group(s), whereas after methyl group shift the label should have been found in the 2-position of **3d***·H$^+$ and finally in the acetic acid *(Scheme 2)*. Thus at lower pH too, **1d** is rearranged exclusively *via* an ester-group migration. Based on the results with labelled **1b** and **1d** at high and low basicity, we suppose that **1c** also undergoes only a COOR$^-$- and/or COO$^-$-group shift rather than a CH_3 shift.

When the reaction of **1c** with aqueous alkali at pH ≈ 10 was followed by ^{1}H-NMR spectroscopy, the signals of the CH_3CO and COO(i-Pr) groups disappeared simultaneously, which means that rearrangement and hydrolysis of the ester group take place concurrently with similar rate. At the same pH, the ethyl ester **1b** was hydrolyzed preferentially prior to rearrangement [3]; it is reasonable that the COO(i-Pr) group is hydrolyzed slower than COOEt, so that the shift reaction can compete. On the other hand, the non-hydrolyzable COO(*t*-Bu) group migrates intact [6].

Kinetics. – Because of extensive hydration the typical UV band of α-dicarbonyls at 400 nm is absent. Therefore, the reactions were followed by measuring the intensity of the UV absorption of the (non-conjugated) carbonyl group (C(3)=O) at 290 nm; in going from H_2O to aqueous K_2CO_3 solution (pH ≈ 10), the band is shifted from 290 to 300 nm, and the extinction coefficient ε rises from *ca.* 50 to *ca.* 150. This is probably due to the formation of the hydrate anion **5**: as carbonyl hydrates stabilized by electron-attracting groups have a pK_a of *ca.* 10 [8], the hydrate-anion concentration in alkaline solutions must be appreciable. In working at a fixed λ = 290 nm, we obtained kinetic curves which were of the first order over at least 2 half-lives (exceptions: see below). As before [3], we performed measurements at 40.2° in two pH regions: between 8 and 10 (defined by $KHCO_3/K_2CO_3$ mixtures of varying composition) and between 12.5 and 13.5 (KOH/KCl mixtures). Following the reaction of the *tert*-butyl ester **1d**, we observed a linear increase of $k_{obs.}$ with [HO$^-$] at the lowest basicities used ('pH' 8.5–9.2); one can estimate[5]) a second order rate constant $k_{rearr.}$ of about 36$M^{-1}s^{-1}$. At higher alkali concentration, the $k_{obs.}$/[HO$^-$] curve flattens off and nearly reaches a

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[5]) [HO$^-$] for calculating $k_{rearr.} = k_{obs.}/[HO^-]$ was taken from measurements of apparent pH ('pH'), which introduces some uncertainty concerning the absolute values of $k_{rearr.}$.

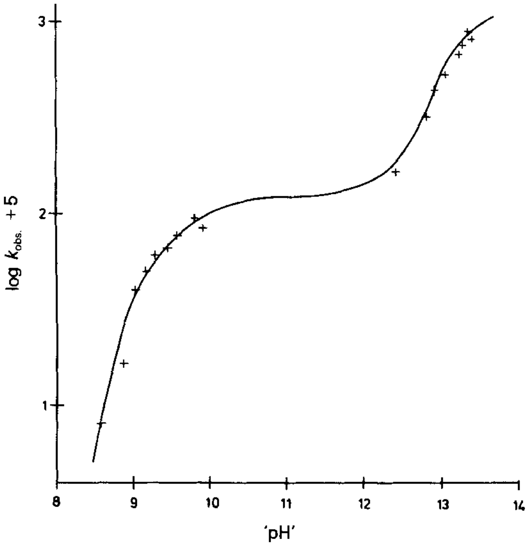

Figure. *Rearrangement of* **1d**: $k_{obs.}$ *as a function of pH*

Table 1. *First Order Rate Constants for the Rearrangement of* **1d**. t = 40.2°; UV measurements at 288 nm in H_2O.

'pH'[a]	$10^3\,k_{obs.}$ [s^{-1}]		'pH'[a]	$10^3\,k_{obs.}$ [s^{-1}]	
8.58	0.08		10.25	1.00	
	0.09	0.08		1.22	
8.87	0.20			1.16	1.13
	0.16		12.42	15.5	
	0.16	0.17		17.3	
9.05	0.42			16.2	16.3
	0.37		12.82	30	
	0.42	0.40		32	31
9.19	0.52		12.88	46	
	0.51			43	
	0.56	0.53		41	43
9.31	0.60		13.01	54	
	0.60			51	52
	0.60	0.60	13.19	67	
9.47	0.63			64	
	0.69			65	65
	0.68	0.66	13.25	75	
9.57	0.78			73	74
	0.75		13.35	87	
	0.78	0.77		86	86
9.80	0.77		13.38	83	
	0.94			74	
	1.06	0.93		77	78
9.88	0.77		13.42	84	
	0.90			92	
	0.82	0.83		83	86

[a] Initial 'pH' determined at 40.2°.

shoulder; the latter might be situated at 'pH' *ca.* 11.5 with a value of $k_{\text{obs.}}$ *ca.* $12 \cdot 10^{-4}\text{s}^{-1}$. In the higher pH range, there is a new increase of $k_{\text{obs.}}$ proportional to [HO$^-$]; if one evaluates [HO$^-$] from the measured 'pH' values, one can estimate $k_{\text{rearr.}} = 0.52\text{M}^{-1}\text{s}^{-1}$ (*Figure* and *Table 1*). It is not possible to decide whether an observed deviation from linearity of the points at highest alkali concentrations is due to difficulties in the pH measurement or to a second flattening of the $k_{\text{obs.}}$/[HO$^-$] profile.

A similar result had been found [3] with the ethyl ester **1b** with $k_{\text{rearr.}} = 26\text{M}^{-1}\text{s}^{-1}$ in the lower pH region and $k_{\text{rearr.}} = 4.4\text{M}^{-1}\text{s}^{-1}$ in the higher one (all measurements at the same temperature as for **1d**). The intermediate flattening at pH 10.5 to 11.5 with $k_{\text{obs.}} > 3 \cdot 10^{-3}\text{s}^{-1}$ had been inferred from the pH profile, but not identified.

As might be anticipated, the isopropyl ester **1c** situates itself between the *tert*-butyl and the ethyl esters: In the lower pH range, an increase of $k_{\text{obs.}}$ proportional to [HO$^-$] with $k_{\text{rearr.}}$ *ca.* $35\text{M}^{-1}\text{s}^{-1}$[6]), followed by a levelling-off which is estimated to reach a plateau at 'pH' *ca.* 11 with $k_{\text{obs.}}$ *ca.* $3.5 \cdot 10^{-3}\text{s}^{-1}$, and in the higher pH range $k_{\text{rearr.}} = 0.96\text{M}^{-1}\text{s}^{-1}$ *(Table 2)*.

Table 2. *First Order Rate Constants for the Rearrangement of* **1c**. t = 40.2°; UV measurements at 288 nm in H_2O.

'pH'[a]	$10^3 k_{\text{obs.}}$ [s^{-1}]		'pH'[a]	$10^3 k_{\text{obs.}}$ [s^{-1}]	
8.72	0.17		10.25	2.55	
	0.14	0.16		2.50	
8.97	0.27			2.52	2.52
	0.32	0.29			
9.11	0.45		12.46	34	
	0.42			33	
	0.48	0.45		32	33
9.19	0.54		12.76	56	
	0.57			47	
	0.61	0.57		57	53
9.31	0.77		12.95	85	
	0.77			80	82
	0.77	0.77	13.03	108	
9.47	0.96			100	
	0.73			123	110
	1.01	0.90	13.15	139	
9.57	1.22			125	
	1.29			119	128
	1.19	1.23	13.26	158	
9.80	1.56			154	
	1.62			156	156
	1.68	1.62	13.45	167	
9.88	1.97			180	173
	1.97	1.97	13.47	177	
				186	
				175	179

[a]) Initial 'pH' determined at 40.2°.

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[6]) As the tangent to the pH profile is necessarily arbitrary, the differences in $k_{\text{rearr.}}$ values in this pH range cannot be considered to be significant.

The existence of a plateau in the $k/[HO^-]$ rate profile has been confirmed with another substrate, ethyl 3-cyclopropyl-2,3-dioxopropionate (**4**).

$$C_3H_5{-}CO{-}C(OH)_2{-}COOEt \qquad \mathbf{4}$$

As demonstrated [1], **4** shows concurrent COOEt migration and ester hydrolysis (followed by COO^- migration); at high pH, the ester group migrates preferentially, whereas at lower pH (*ca.* 10), hydrolysis is more rapid than rearrangement. Kinetic measurements had shown that at 'pH' 12.1–12.7, the rate of rearrangement increases with increasing $[HO^-]$ yielding a second order rate constant $k_{rearr.} = 0.9 M^{-1}s^{-1}$ [1]. We have now extended our measurements to higher base concentrations and found a rate profile similar to that of **1b**: At 'pH' *ca.* 13, the rate is levelling off with a first order rate constant $k_{obs.}$ *ca.* $5.5 \cdot 10^{-2}s^{-1}$; after a narrow plateau, the rate increases again proportional to $[HO^-]$ yielding a second order rate constant $k_{rearr.} = 0.85 M^{-1}s^{-1}$. This is another case where the plateau has been observed directly *(Table 3)*.

Table 3. *First Order Rate Constants for the Rearrangement of* **4**. $t = 40.0°$; UV measurements at 290 nm; H_2O, $\mu = 1.0$.

'pH'[a]	$10^3\,k_{obs.}$ [s^{-1}]	'pH'[a]	$10^3\,k_{obs.}$ [s^{-1}]
12.76	45	13.07	61
12.91	55	13.12	75
12.97	54	13.14	79
13.02	55	13.15	81
13.05	55	13.17	87

[a] Initial 'pH' determined at 40.0°.

Discussion. – The analysis of the data is straightforward for the *tert*-butyl ester **1d** with no ester-group hydrolysis interfering. At 'pH' *ca.* 10, the rate increases with increasing concentration of HO^-. This agrees with the generally accepted mechanism for the benzilic-acid rearrangement according to which the hydrate monoanion **5** is the reactive species. In the case of the hydrate **1**, it would be formed by direct proton abstraction and not by HO^- addition as in the case of simpler diketones. The saturation plateau at 'pH' *ca.* 11–12 is attained at complete transformation of **1** to **5**, owing to its acidity (see above); a similar behaviour had been observed in other cases [9]. The second increase of $k_{obs.}$ with increasing $[HO^-]$ would then correspond to the formation of the dianion $CH_3{-}CO{-}C(O^-)_2{-}COOR$ (**6**); this is a substrate even more favourable for rearrangement, for it yields directly the rearranged carboxylate anion **3**, whereas the rearrangement of **5** gives the carboxylic acid first, with less stabilization by resonance. On the other hand, the preequilibrium $\mathbf{5} \rightleftarrows \mathbf{6}$ must show a less favourable pK_a than that of the first dissociation $\mathbf{1} \rightleftarrows \mathbf{5}$. As a result of these two conflicting influences, we see a nearly 70fold decrease in velocity, $k_{rearr.}$ passing from $36 M^{-1}s^{-1}$ to $0.5 M^{-1}s^{-1}$.

The ethyl and isopropyl esters **1b** and **1c** react, in the high pH region, also by the ester-group-shift mechanism. The similarity in the rate profiles suggests that here too the dianion **6** is rearranged. The rate constant of the ethyl ester is slightly higher than those of the isopropyl and the *tert*-butyl esters, which is explicable in terms of steric effects.

In the lower pH region, the situation is complicated by the existence of the simultaneous and somewhat prevalent route *via* ester hydrolysis followed by (rate-determining) carboxylate-group migration [3]. One can assume that the COO^- group, more electron-rich than COOR, has a greater inherent tendency for migration towards an electron-deficient center. On the other hand, the presence of the negative charge on the carboxylate diminishes the acidity of the diol group and, by decreasing the diolate concentration, slows the rearrangement reaction down. The two opposing effects happen to compensate one another, so that the rate constant $k_{\text{rearr.}}$ of **1b** in the low pH range is quite close to that of the *tert*-butyl ester **1d** (26 and $36 \text{M}^{-1}\text{s}^{-1}$, resp.)[6]. The rate of the carboxylate-group shift shows a saturation phenomenon analogous to that of the ester-group migration; the measurements do not allow to locate it with sufficient precision. As in the case of the carboxylate-group shift the starting material for the rearrangement is accumulating during the preceding, more rapid step of hydrolysis, one cannot assume the individual run to be first order. Indeed, we observed that in these kinetic runs first order plots were of restricted validity [1] [3].

The isopropyl ester **1c** would be expected to be intermediate between the ethyl and the *tert*-butyl esters. As these did not furnish very different rate values, the isopropyl *k* values are rather close too.

Compound **4**, a (hydrolyzable) ethyl ester in which the electron-donating cyclopropyl group diminishes the basicity of the diol as well as the electrophilicity of the carbonyl group at C(3), would be expected to show a smaller $k_{\text{rearr.}}$ than **1b** for the ethyl ester group migration at high pH and for the carboxylate migration at lower pH, and a saturation value situated at higher pH. All these expectations have been confirmed by the measurements (see above).

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Experimental Part

General Remarks. See [3]. Radioactivity measurements: Institut de Radiophysique Appliquée, Lausanne, with a *Packard Tricarb 3380* instrument.

Isopropyl α,β-Dioxobutyrate (Hydrated; **1c***).* To isopropyl acetoacetate (77.0 g, 0.50 mol) in AcOH (80 ml) was added dropwise at 0° at soln. of $NaNO_2$ (38.5 g, 0.56 mol) in H_2O (77 ml). The mixture was stirred for 2 h at 0° and 4 h at r.t., neutralized, and extracted with Et_2O. The Et_2O extract was dried over Na_2SO_4, the solv. removed under reduced pressure, and the residue dissolved in $CHCl_3$ (100 ml). At –25°, N_2O_4 (9.3 g, 0.15 mol) was slowly added; the mixture was kept 12 h at –25°, 15 h at –15°, 24 h at 0°, and 3 days at r.t. and was several times distilled under reduced pressure: 15.2 g (17%) of a yellow oil, b.p. 75–78°/10 Torr. Exposed to moist air, colourless crystals were formed; recrystallized from Et_2O/petroleum ether, m.p. 83° (hemihydrate). IR (KBr): 3425, 3360 (OH); 1735, 1710 (CO). ^{1}H-NMR (in D_2O, freshly prepared soln.; AcOH as internal standard): 5.13 (*m*, $CHMe_2$); 2.34 (*s*, CH_3CO); 1.84 (*s*, < 1H, MeC(OH)O–); 1.29 (*d*, $J = 7$, $(CH_3)_2C$); after some days standing, the peak at 1.84 disappears. Anal. calc. for $C_7H_{10}O_4 \cdot \frac{1}{2} H_2O$ (167.2): C 50.29, H 6.63; found: C 50.24, H 6.56.

Rearrangement of **1c**. a) *At pH* ca. *14.* A mixture of **1c** (solid hydrate; 1.6 g, 5 mmol) and 2N NaOH (20 ml) was left for 1 h at r.t. The soln. was slightly acidified and concentrated under reduced pressure and the residue extracted with Et_2O yielding 1.1 g (82%) of *2-methyltartronic acid*, m.p. 133–135°.

b) *At pH* ca. *9.* A mixture of **1c** (1.6 g) and sat. $KHCO_3/K_2CO_3$ 1:1 buffer (50 ml) was kept for 3 days at r.t. Workup as under *a*) yielded 0.95 g (73%) of *2-methyltartronic acid.*

Rearrangement of tert-*Butyl α,β-Dioxo[2-^{14}C]butyrate* (**1d***) *at pH* ca. *9.0.* A mixture of **1d*** (1.4 g, 7.4 mmol; spec. activity = 59.3 nCi/mmol) [5] and $KHCO_3/K_2CO_3$ buffer (pH *ca.* 9; 50 ml) was kept 3 days at r.t. The mixture was slightly acidified with HCl and concentrated under reduced pressure. The residue was extracted with Et_2O, the Et_2O dried and evaporated, and the residue crystallized from benzene: 1.0 g (72%) of tert-*butyl hydrogen 2-methyl[^{14}C]tartronate* (**3d***·H^+) of m.p. 84–86°, identical with authentic material [6]; specific activity = 54.8 ± 2 nCi/mmol.

To determine the position of the label, **3d***·H^+ was hydrolyzed and decarboxylated by heating with *ca.* 3N HCl at 110°. *[^{14}C]CO$_2$* was quantitatively collected in a 12% soln. of 2-aminoethanol in MeOH; it showed spec. activity = 20.3 ± 2 nCi/mmol. From the aq. soln. *[^{14}C]lactic acid* was isolated by continuous extraction with Et_2O, which was dried and evaporated; the residue was distilled *in vacuo* (b.p. 122°/15 Torr). The [^{14}C]lactic acid was heated with 30% H_2O_2 (5 ml) for 9 h at 110°; [^{14}C]CO$_2$ was collected in a 12% soln. of 2-aminoethanol in MeOH; it showed spec. activity = 22.7 ± 2 nCi/mmol[7]). From the residual soln., *AcOH* was isolated as described [6] and transformed into the *p*-bromophenacyl ester; spec. activity = 0.44 ± 0.05 nCi/mmol.

Kinetics. Method: See [3]. *Solutions:* For the low pH range, 0.67M K_2CO_3 (a) and 1.33M $KHCO_3$ containing 0.67M KCl (b) were mixed at various volume ratios. For the high pH range, 2M KOH was mixed with 2M KCl at various volume ratios. The aq. substrate solns. were 0.0099M **1c**, 0.0086M **1d** (calculated as monomer), and 0.020M **4** [1]. All solutions were pre-thermostatted to 40.2° and 40.0°, resp. For each kinetic run, 1.5 ml of buffer soln. in a UV cuvette were mixed with 1.5 ml of the substrate soln. The intensity at 288 and 290 nm, resp., was followed. 'pH' was determined in parallel runs under the same conditions (40.2 and 40.0°, resp.) with a combined glass electrode. Results: see *Tables 1–3.*

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[7]) The loss of specific activity is attributed to partial decarboxylation of AcOH.