Photolysis of Alkoxyacetic Acids in the presence of Mercury(II) Oxide and Iodine

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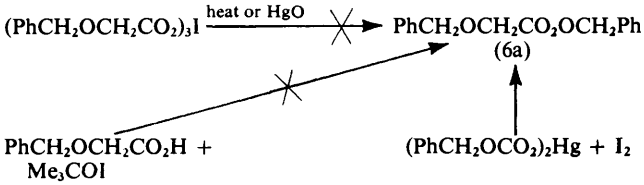
Homolytic decarboxylation of a series of alkoxyacetic acids has furnished alkoxyalkyl alkoxyacetates when no substituents were present at the 2-position. Electron donating and withdrawing 2-substituents, with the exception of trichloromethyl, afforded products due to fragmentation of the alkoxyacetic acids. The reaction pathway is rationalised on the basis of the reactivity of the alkoxyalkyl iodide intermediates.

Free radicals are commonly observed to undergo fragmentation leading to elimination of a stable fragment. The gas phase reactions [1] have been well documented and relative rate constants obtained for a variety of reactions in solution.[2] Even though elimination of stable molecules from free radicals [3] is a well established process in synthesis, secondary fragmentation of the radical to generate a third radical has not been extensively investigated. Examples include the decomposition of α-hydroxy acids [4] in a one electron oxidation process and homolytic bridgehead substitution which has been effected by the decomposition of oxalate half esters [5] and carbazates.[6] The relatively inaccessible iminyl radical was obtained by persulphate oxidation of oximino-acetic acids [7] and alkenes have been formed by a secondary fragmentation of tetra-alkyltin radicals.[8] More recently this concept has been used for decarboxylations of esters containing vicinal chloro or thiophenyl groups with tri-n-butylstannane.[9] This paper reports on the decarboxylation of 2-alkoxyacetic acids with mercury(II) oxide and iodine.

It was envisaged that homolytic decarboxylation of 2-alkoxyacetic acids (1) would either produce an intermediate alkyloxyalkyl radical (3) or that a concerted decomposition to give an alkyl radical and a carbonyl fragment would occur. Aryloxymethyl radicals generated from aryloxyacetic acids [10] as expected do not eliminate methanal but undergo reactions with *ortho*-substituents, and flavin-mediated photodecarboxylations [11] of phenoxy- and thiophenoxy-acetic acids afford phenoxy- and thiophenoxy-methyl radicals which add to the flavanoenzyme.

In order to investigate the behaviour of alkoxyalkyl radicals, benzyloxyacetic acid (1a) was irradiated in aprotic solvents in the presence of mercury(II) oxide and iodine which is an effective positive iodinating reagent.[5] With carbon tetrachloride or benzene as solvents the only product was benzyloxymethyl benzyloxyacetate (6a).

It is proposed that benzyloxymethyl benzyloxyacetate (6a) is formed by reaction of mercury benzyloxyacetate and benzyloxymethyl iodide (4a), which is formed by decarboxylation of the acid (1a), and the radical (3a) is then trapped by iodine.[13] The participation of mercury benzyloxyacetate in ester (6a) formation was indicated by the production of a different ester, *viz.* benzyl benzyloxyacetate, when benzyloxyacetic acid (1a) was irradiated in the presence of a filtered carbon tetrachloride solution of mercury(II) oxide and excess of iodine which is devoid of mercury salts.[14] Furthermore the formation of mixed t-butyl acetals (10) as the major and only product from the decarboxylation reactions of benzyloxyacetic acid (1a) and isopropyloxyacetic acid (1d), respectively, when these acids were irradiated in the presence of t-butyl hypoiodite [15] (generated from potassium t-butoxide and iodine monochloride) lends support to the proposal that mercury carboxylates participate in ester (6) formation. The



Scheme 1.

low yield of ester (6a) produced in the reaction of benzyloxyacetic acid with t-butyl hypoiodite is probably formed by a different pathway. These experiments also serve to eliminate the intervention of iodine triacylates,[16] which form esters upon thermal decomposition or by reaction with mercury(II) oxide, as intermediates in the formation of alkoxyalkyl alkoxyacetates (6). Iodine triacylates could be envisaged to be formed in the reaction with t-butyl hypoiodite but no ester (6a) was produced under these conditions (Scheme 1). However ester (6a) is produced when mercury benzyloxyacetate reacts with iodine and these reaction conditions cannot be considered to be more oxidative.

Since the mercury benzyloxyacetate is stable to the irradiation, and decarboxylation was effected by irradiation of benzyloxyacetic acid (1a) in the presence of t-butyl hypoiodite as well as the filtered mercury(II) oxide and iodine solution, the mercury benzyloxyacetate is first converted into the acyl hypoiodite which upon irradiation generates the benzyloxyacetoxy radical (2a). This species readily eliminates carbon dioxide to form the benzyloxymethyl radical (3a) which is trapped by iodine [13] to generate the iodo ether (4a). The formation of benzyloxymethyl benzyloxyacetate (6a) is clear evidence that the acyl hypoiodite does not undergo a concerted decomposition in which carbon dioxide and formaldehyde are eliminated [equation (1)].

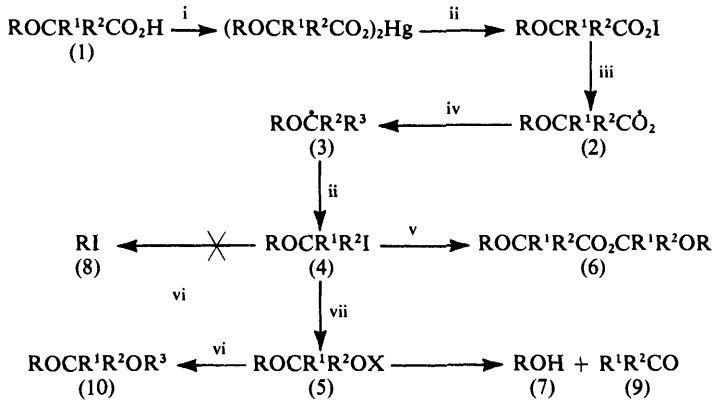
$$\underset{(6a)}{PhCH_2OCH_2C\dot{O}_2} \not\longrightarrow Ph\dot{C}H_2 + HCHO + CO_2 \quad (1)$$

Since benzyloxyacetic acid (1a) upon reaction with mercury(II) oxide and iodine could generate either water, hypoiodous acid, or iodine monoxide [equations (2), (3), and (4)] it is conceivable that mercury benzyloxyacetate could react with either the iodo ether (4a) or a hemiacetal derivative

$$PhCH_2OCH_2CO_2H + HgO \longrightarrow (PhCH_2OCH_2CO_2)_2Hg + H_2O \quad (2)$$

$$HgO + 2\,I_2 \longrightarrow I_2O + HgI_2 \quad (3)$$

$$I_2O + H_2O \longrightarrow 2\,HOI \quad (4)$$



Scheme 2. i, HgO; ii, I_2; iii, *hν*; iv, $-CO_2$; v, $(ROCR^1R^2CO_2)_2Hg$; vi, R^3OH; vii, HOX

Table. Products from the reaction of alkyloxyacetic acids (1a—q)

Acid	R	R^1	R^2	Products (%)
(1a)	$PhCH_2$ *	H	H	6 (100)
(1b)	C_6H_{13}	H	H	6 (98)
(1c)	Et	H	H	6 (59), 1 (40)
(1d)	Pr^i	H	H	6 (90)
(1e)	*p*-$MeC_6H_4CH_2$	H	H	6 (75)
(1f)	*p*-$ClC_6H_4CH_2$	H	H	6 (92)
(1g)	*p*-$MeC_6H_4CH_2$	H	H	6 (91)
(1h)	$PhCH_2$	Me	H	7 (48), 1 (52)
(1i)	Pr^i	Me	H	7 (82), 9 (75)
(1j)	$PhCH_2$	Me	Me	7 (80)
(1k)	Et	Ph	H	9 (55), 10 (31)
(1l)	Et	*p*-$MeOC_6H_4$	H	9 (40), 10 (60)
(1m)	Et	*p*-MeC_6H_4	H	9 (50), 10 (50)
(1n)	Et	*p*-$O_2NC_6H_4$	H	9 (30), 10 (18), 1 (35)
(1o)	Et	Cl_3C	H	6 (65)
(1p)	Bu^t	H	H	6 (75)
(1q)	Ph	H	H	6 (100)

* Solvent benzene and carbon tetrachloride.

(5a), which is derived from the iodo ether by reaction with either of the above oxygen containing species, to form the ester (6a). However, since irradiation of mercury benzyloxyacetate in the presence of iodine gave the ester (6a) and this reaction mixture does not contain species which could generate the hemiacetal derivatives (5a), the ester (6a) is in all probability generated by reaction of the iodo ether (4a) and mercury benzyloxyacetate. This proposal is in accord with the proposed pathway [17] for the formation of esters [4] in the Cristol and Firth [18] modification of the Hunsdiecker reaction in which esters are produced when carboxylic acids are decarboxylated with mercury(II) oxide and bromine.

The effect of substituents and the structure of the alkoxyacetic acids was investigated (Table). Surprisingly, variation of the alkyl group R had no significant effect on ester formation. Hence it is concluded that structural or electronic effects of the group R neither facilitate homolytic fragmentation of the intermediate radical (3) in competition with trapping of the radical by iodine nor promote heterolysis of the iodo ether (4).

However, substituents R^1 and/or R^2 at the 2-position of the alkoxyacetic acid (1) had a pronounced effect on the reaction. Mono- or di-methyl substituents induced fragmentation to the alcohol (7) and the aldehyde or ketone (9) [equation (5)]. The

$$EtOCR^1R^2OH \longrightarrow EtOH + R^1R^2C{=}O \longleftarrow\!\!\times\!\!- EtOCR^1R^2I \quad (5)$$

formation of alcohols and the absence of the iodides (8), which are relatively stable under the reaction conditions, indicates that the secondary fragmentation is a heterolytic process involving either the iodo ether (4) or the hemiacetal species (5). With trichloromethyl as the 2-substituent it was found that the major product from (1o) was the ester (6) whereas phenyl anisyl, *p*-tolyl, and *p*-nitrophenyl groups at the 2-position [compounds (1l), (1m), and (1n)] afforded the corresponding aldehydes (9), due to the secondary fragmentation process, and diethyl acetals (10) of the aldehydes. The diethyl acetals (10) could be formed from the aldehydes and ethanol fragments since benzyl alcohol reacted with acetaldehyde under the reaction conditions to form the dibenzyl acetal. However, it is more likely that the acetals (10) are being formed by reaction of the iodo ether (4), or the hemiacetal species (5) and ethanol generated in the reaction mixture since in the reaction with t-butyl hypoiodite only the mixed acetal was produced. The ethanol is in all probability generated by decomposition of a hemiacetal species (5) and not from the iodo ether since no other products arising from nucleophilic attack on the alkyl group R were detected.

These results are compatible with the reaction sequences outlined in Scheme 2. Initially there is a rapid formation of the mercury salt of the acid which slowly forms the acyl hypoiodite. Irradiation effects homolysis of the O–I bond to produce the acyloxy radical (2) which eliminates carbon dioxide. The alkoxyalkyl radical is trapped by iodine and the iodo ether (4) which subsequently reacts either with unchanged carboxylate to form the ester (6) or with an oxygen species to form the hemiacetal derivative (5). Decomposition of the hemiacetal species (5) would afford the products attributed to the secondary fragmentation process, and the alcohol derived in some cases reacts with either the iodo ether (4) or the hemiacetal species (5) to afford the more stable acetal (10).

Substituents on the 2-position, with the exception of trichloromethyl, prevent ester formation. This is mainly due to a steric effect since aryl groups containing electron withdrawing and donating substituents gave similar products. The formation of ester (6) as the main product in the reaction of ethoxy(trichloromethyl)acetic acid (10) could be due to enhanced stability of the derived iodo ether, or to less steric

hindrance than in the case of the 2-*p*-nitrophenyl substituent, or to a higher concentration of the mercury carboxylate in the solvent. The heterogenous nature of the reaction prevents relative rate investigations from which mechanistic details may be derived.

Experimental

^{1}H N.m.r. spectra were recorded on a 60 MHz Perkin-Elmer R12A spectrometer with tetramethylsilane as internal standard. I.r. spectra were measured with a Perkin-Elmer 297 spectrometer. Mercury was determined by ethylenediaminetetraacetic acid (EDTA) titration in a Metrohm Herisau Potentiograph E 536. Ether refers to diethyl ether throughout.

General Procedure for Synthesis of Alkoxyacetic Acids.—(i) With water-insoluble alcohols, the alcohol (0.2 mol) in benzene (200 ml) was treated with sodium hydride (0.4 mol) for 1 h, then with chloroacetic acid (0.2 mol) and heated under reflux for 1 h. The reaction mixture was poured into water, separated and washed with ether, acidified (conc. HCl), extracted ($CHCl_3$), dried (Na_2SO_4) and concentrated. The acid product was either distilled or crystallized.

(ii) With water-soluble alcohols, the alcohol (200 ml) was treated with sodium hydride (0.4 mol), and then treated and worked up as above.

The following acids were thus obtained.

(*a*) Benzyloxyacetic acid (1a) (0.07 mol), b.p. 175 °C/0.3 mmHg (lit.,[19] 136 °C/0.2 mmHg); $\nu_{max.}$ (film) 1 720 cm^{-1}; $\delta(CCl_4)$ 4.04 (2 H, s), 4.53 (2 H, s), 7.22 (5 H, s), and 10.9 (1 H, s).

(*b*) *Hexyloxyacetic acid* (1b) (0.14 mol), b.p. 155 °C/1.5 mmHg; $\nu_{max.}$ (film) 1 740 cm^{-1}; $\delta(CCl_4)$ 1.3 (11 H, m), 3.5 (2 H, t, *J* 6 Hz), 4.0 (2 H, s), and 10.2 (1 H, s) (Found: C, 60.2; H, 10.1. $C_8H_{16}O_3$ requires C, 59.9; H, 10.1%).

(*c*) Ethoxyacetic acid (1c) (0.05 mol), b.p. 73 °C/0.7 mmHg (lit.,[20] 97 °C/7 mmHg); $\nu_{max.}$ (film) 1 740 cm^{-1}; $\delta(CCl_4)$ 1.23 (3 H, t, *J* 7.3 Hz), 3.6 (2 H, q, *J* 3 Hz), 4.07 (2 H, s), and 10.8 (1 H, s).

(*d*) Isopropoxyacetic acid (1d) (0.12 mol), b.p. 125 °C/1.0 mmHg (lit.,[20] 97—101 °C/5 mmHg); $\nu_{max.}$ (film) 1 730 cm^{-1}; $\delta(CCl_4)$ 1.15 (6 H, d, *J* 6 Hz), 3.7 (1 H, septet, *J* 6 Hz), 4.05 (2 H, s), and 8.3 (1 H, s).

(*e*) p-*Methylbenzyloxyacetic acid* (1e) (0.2 mol), recrystallized from benzene–hexane had m.p. 49—51 °C; $\nu_{max.}$ ($CHCl_3$) 1 740 cm^{-1}; $\delta(CDCl_3)$ 2.3 (3 H, s), 4.0 (2 H, s), 4.5 (2 H, s), 7.12 (4 H, s), and 11.14 (1 H, s) (Found: C, 66.3; H, 6.8. $C_{10}H_{12}O_3$ requires C, 66.6; H, 6.7%).

(*f*) *p*-Chlorobenzyloxyacetic acid (1f) (0.08 mol), recrystallized from benzene–light petroleum (b.p. 40—60 °C) had m.p. 70—75 °C (lit.,[19] 74 °C); $\nu_{max.}$ ($CHCl_3$) 1 730 cm^{-1}; $\delta(CDCl_3)$ 4.15 (2 H, s), 4.6 (2 H, s), 7.3 (4 H, s), and 10.8 (1 H, s) (Found: C, 53.9; H, 4.6. Calc. for $C_9H_9ClO_3$: C, 53.9; H, 4.6%).

(*g*) *p*-Methoxybenzyloxyacetic acid (1g) (0.2 mol), recrystallized from benzene–hexane, had m.p. 49—52 °C (lit.,[19] 53 °C); $\nu_{max.}$ ($CHCl_3$) 1 730 cm^{-1}; $\delta(CDCl_3)$ 3.75 (3 H, s), 4.05 (2 H, s), 4.5 (2 H, s), 6.86 (2 H, d, *J* 9.3 Hz), 7.29 (2 H, d, *J* 9.3 Hz), and 8.75 (1 H, s) (Found: C, 61.5; H, 6.2. Calc. for $C_{10}H_{12}O_4$: C, 61.2; H, 6.2%).

(*h*) 2-*Benzyloxypropionic acid* (1h) (0.2 mol), recrystallized from light petroleum (b.p. 40—60 °C), had m.p. 47—48 °C; $\nu_{max.}$ ($CHCl_3$) 1 725 cm^{-1}; $\delta(CDCl_3)$ 1.45 (3 H, d, *J* 6.9 Hz), 4.05 (1 H, q, *J* 6.9 Hz), 4.55 (2 H, dd, *J* 11, 2 Hz), 7.3 (5 H, s), and 11.35 (1 H, s) (Found: C, 66.5; H, 6.7. $C_{10}H_{12}O_3$ requires C, 66.6; H, 6.7%).

(*i*) 2-*Isopropoxypropionic acid* (1i) (0.18 mol), b.p. 90 °C/0.5 mmHg; $\nu_{max.}$ ($CHCl_3$) 1 720 cm^{-1}; $\delta(CCl_4)$ 1.15 (3 H, d, *J* 5.3 Hz), 1.19 (3 H, d, *J* 5.3 Hz), 1.38 (3 H, d, *J* 6.7 Hz), 3.7 (1 H, dq, *J* 5.3 Hz), 4.05 (1 H, q, *J* 6.7 Hz), and 11.15 (1 H, s).

(*j*) 2-Benzyloxy-2-methylpropionic acid (1j), synthesized by a published procedure,[21] b.p. 150 °C/0.2 mmHg; $\nu_{max.}$ (film) 1 710 cm^{-1}; $\delta(CCl_4)$ 1.5 (6 H, s), 4.47 (2 H, s), 7.2 (5 H, s), and 11.27 (1 H, s) (Found: C, 68.0; H, 7.1. Calc. for $C_{11}O_{14}O_3$: C, 68.0; H, 7.3%).

(*k*) *Ethoxy(phenyl)acetic acid* (1k). Ethyl mandelate (30 g, 0.167 mol) in benzene (100 ml) was treated with sodium hydride (8 g, 0.33 mol) for 1 h and then heated with ethyl bromide (18.2 g, 0.16 mol) for 16 h. Work-up as before gave ethoxy(phenyl)acetic acid (10.6 g, 0.06 mol), b.p. 160 °C/2.5 mmHg (lit.,[22] 140—145 °C); $\nu_{max.}$ (film) 1 730 cm^{-1}; $\delta(CCl_4)$ 1.15 (3 H, t, *J* 6.7 Hz), 3.45 (2 H, q, *J* 6.7 Hz), 4.75 (1 H, s), 7.3 (5 H, m), and 10.6 (1 H, s).

(*l*) *Ethoxy*-p-*methoxyphenylacetic acid* (1l). Ethyl *p*-methoxymandelate (synthesized from *p*-methoxybenzaldehyde and sodium cyanide [23]) was converted into the sodium salt with excess of sodium hydride and heated with ethyl bromide in benzene for 12 h. The acid, separated as before, was converted into the *S*-benzylthiouronium salt which was recrystallized and hydrolysed to give ethoxy-*p*-methoxyphenylacetic acid, b.p. 170—174 °C/0.5 mmHg (lit.,[20] 166—170 °C/1.5 mmHg); $\nu_{max.}$ (film) 1 720 cm^{-1}; $\delta(CCl_4)$ 1.15 (3 H, t, *J* 7 Hz), 3.4 (2 H, q, *J* 7 Hz), 3.65 (3 H, s), 4.7 (1 H, s), 6.75 (2 H, d, *J* 8.7 Hz), 7.3 (2 H, d, *J* 8.7 Hz), and 11.2 (1 H, s).

(*m*) *Ethoxy*-p-*methylphenylacetic acid* (1m). Ethyl *p*-methylmandelate (synthesized from *p*-tolualdehyde and potassium cyanide [24]) was treated and purified in the same manner as for *p*-methoxyphenylacetic acid and gave ethoxy-*p*-methylphenylacetic acid, b.p. 160—165 °C/0.6 mmHg (lit.,[20] 125—127 °C/0.1 mmHg); $\nu_{max.}$ (film) 1 720 cm^{-1}; $\delta(CCl_4)$ 1.2 (3 H, t, *J* 7.3 Hz), 2.3 (3 H, s), 3.45 (2 H, q, *J* 7.3 Hz), 4.62 (1 H, s), 7.05 (2 H, d, *J* 8.3 Hz), 7.3 (2 H, d, *J* 8.3 Hz), and 10.0 (1 H, s) (Found: C, 67.5; H, 7.3. Calc. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.3%).

(*n*) Ethoxy-*p*-nitrophenylacetic acid (1n), synthesized by a published procedure; [25] $\nu_{max.}$ (film) 1 725 cm^{-1}; $\delta(CDCl_3)$ 1.27 (3 H, t, *J* 7 Hz), 3.62 (2 H, q, *J* 7 Hz), 5.0 (1 H, s), 7.6 (2 H, d, *J* 9.3 Hz), 8.2 (2 H, d, *J* 9.3 Hz), and 9.45 (1 H, s).

(*o*) Ethoxy(trichloromethyl)acetic acid (1o), synthesized by a published procedure,[26] b.p. 107—108 °C/0.8 mmHg (lit.,[25] 115 °C/0.2 mmHg); $\nu_{max.}$ (film) 1 730 cm^{-1}; $\delta(CCl_4)$ 1.3 (3 H, t, *J* 6.7 Hz), 3.75 (2 H, q, *J* 6.7 Hz), 4.2 (1 H, s), and 10.75 (1 H, s).

(*p*) t-Butoxyacetic acid (1p) (0.06 mol), b.p. 96.8 °C/0.2 mmHg (lit.,[27] 104—106 °C/12 mmHg); $\nu_{max.}$ (film) 1 730 cm^{-1}; $\delta(CCl_4)$ 1.2 (9 H, s), 4.0 (2 H, s), and 10.0 (1 H, s).

Mercury(II) *Benzyloxyacetate.*—The mercury salt was synthesized by stirring benzyloxyacetic acid (4.2 g) with mercury(II) oxide (4 g) in carbon tetrachloride (50 ml) for 0.5 h. The mixture was filtered, dried (Na_2SO_4) and concentrated to a white solid of *mercury*(II) *benzyloxyacetate*, m.p. 110—113 °C; $\nu_{max.}$ (Nujol) 1 600 cm^{-1}; $\delta(CDCl_3)$ 4.05 (4 H, s), 4.56 (4 H, s), and 7.3 (10 H, s) (Found: Hg, 37.1. $C_{18}H_{18}HgO_6$ requires Hg, 37.7%).

Mercury(II) *Ethoxyacetate.*—*Mercury*(II) *ethoxyacetate* was synthesized from ethoxyacetic acid as above, m.p. 135—137 °C; $\nu_{max.}$ (Nujol) 1 600 cm^{-1}; $\delta(CDCl_3)$ 1.3 (6 H, t, *J* 6.8 Hz), 3.55 (4 H, q, *J* 6.8 Hz), and 4.05 (4 H, s) [Found: Hg, 49.7. $(C_4H_7O_3)_2Hg$ requires Hg, 49.33%].

General Procedure for the Irradiation of Carboxylic Acids in the Presence of Mercury(II) *Oxide and Iodine.*—The alkoxyacetic acid (1×10^{-2} mol) in carbon tetrachloride (100 ml) was treated with iodine (9×10^{-2} mol) and mercuric oxide

(3×10^{-2} mol) in a Pyrex flask kept at ambient temperature, stirred for 5 min and then irradiated with a 1 kW-tungsten lamp for *ca.* 5 h. The reaction mixture was poured into excess of aqueous sodium thiosulphate solution and extracted with chloroform (3×50 ml), dried (Na_2SO_4) and concentrated, distilled (or recrystallized), and analysed (n.m.r., i.r., g.l.c.).

(*a*) Benzyloxyacetic acid (1a) gave *benzyloxymethyl benzyloxyacetate* (6a), b.p. 170—174 °C/0.15 mmHg; $\nu_{max.}$ (film) 1 760 cm^{-1}; $\delta(CCl_4)$ 3.9 (2 H, s), 4.46 (2 H, s), 4.54 (2 H, s), 5.26 (2 H, s), and 7.2 (10 H, s) (Found: C, 71.0; H, 6.1. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.3%).

(*b*) Hexyloxyacetic acid (1b) gave *hexyloxymethyl hexyloxyacetate* (6b), b.p. 178—180 °C/0.8 mmHg; $\nu_{max.}$ (film) 1 760 cm^{-1}; $\delta(CCl_4)$ 0.6—1.6 (22 H, m), 3.46 (2 H, t, *J* 5.5 Hz), 3.57 (2 H, t, *J* 5.4 Hz), 3.95 (2 H, s), and 5.23 (2 H, s) (Found: C, 66.1; H, 11.0. $C_{15}H_{30}O_4$ requires C, 65.7; H, 11.0%).

(*c*) Ethoxyacetic acid (1c) gave *ethoxymethyl ethoxyacetate* (6c), b.p. 80 °C/0.4 mmHg; $\nu_{max.}$ (film) 1 760 cm^{-1}; $\delta(CCl_4)$ 1.2 (6 H, t, *J* 7 Hz), 3.53 (2 H, q, *J* 7 Hz), 3.66 (2 H, q, *J* 7 Hz), 4.0 (2 H, s), and 5.25 (2 H, s) (Found: C, 51.3; H, 8.4. $C_7H_{14}O_4$ requires C, 51.8; H, 8.4%).

(*d*) Isopropoxyacetic acid (1d) gave *isopropoxymethyl isopropoxyacetate* (6d), b.p. 90 °C/0.3 mmHg; $\nu_{max.}$ (film) 1 760 cm^{-1}; $\delta(CCl_4)$ 1.16 (12 H, d, *J* 6 Hz), 3.7 (2 H, septet, *J* 6 Hz), 3.96 (2 H, s), and 5.3 (2 H, s) (Found: C, 56.3; H, 9.8. $C_9H_{18}O_4$ requires C, 56.8; H, 9.5%).

(*e*) *p*-Methylbenzyloxyacetic acid (1e) gave a solid which crystallized from hexane as p-*methylbenzyloxymethyl* p-*methylbenzyloxyacetate* (6e), m.p. 38—41 °C, $\nu_{max.}$ ($CHCl_3$) 1 760 cm^{-1}; $\delta(CCl_4)$ 2.3 (6 H, s), 3.94 (2 H, s), 4.5 (2 H, s), 4.58 (2 H, s), 5.31 (2 H, s), and 7.15 (8 H, s) (Found: C, 72.5; H, 7.1. $C_{19}H_{22}O_4$ requires C, 72.6; H, 7.05%).

(*f*) *p*-Chlorobenzyloxyacetic acid (1f) gave a solid which crystallized from chloroform–light petroleum (40—60 °C) as p-*chlorobenzyloxymethyl* p-*chlorobenzyloxyacetate* (6f), m.p. 61—64 °C; $\nu_{max.}$ ($CHCl_3$) 1 760 cm^{-1}; $\delta(CDCl_3)$ 4.05 (2 H, s), 4.55 (2 H, s), 4.63 (2 H, s), 5.4 (2 H, s), and 7.35 (8 H, s) (Found: C, 56.9; H, 4.5. $C_{17}H_{16}Cl_2O_4$ requires C, 57.4; H, 4.5%).

(*g*) *p*-Methoxybenzyloxyacetic acid (1g) gave a solid which crystallized from benzene–hexane as p-*methoxybenzyloxymethyl* p-*methoxybenzyloxyacetate* (6g), m.p. 58—59.5 °C; $\nu_{max.}$ ($CHCl_3$) 1 760 cm^{-1}; $\delta(CDCl_3)$ 3.7 (6 H, s), 3.94 (2 H, s), 4.48 (2 H, s), 4.52 (2 H, s), 5.3 (2 H, s), 6.78 (2 H, d, *J* 8.1 Hz) and 7.23 (2 H, d, *J* 8.1 Hz) (Found: C, 65.3; H, 6.4. $C_{19}H_{22}O_6$ requires C, 65.9; H, 6.4%).

(*h*) 2-Benzyloxypropionic acid (1h) gave benzyl alcohol (7) (i.r. and n.m.r. identical with an authentic specimen) and starting material.

(*i*) 2-Isopropoxypropionic acid (1i) was worked up as usual and analysed by g.l.c. (Carbowax 20 M on Chromosorb 80—100 mesh; oven: 20 °C, N_2: 30 ml min^{-1}) to yield isopropyl alcohol (7) and acetaldehyde (9).

(*j*) 2-Benzyloxy-2-methylpropionic acid (1j) gave benzaldehyde (9) and benzyl alcohol (7) (n.m.r. and i.r. identical with an authentic specimen).

(*k*) Ethoxy(phenyl)acetic acid (1k) gave benzaldehyde (9) and the diethyl acetal of benzaldehyde (10) (i.r. and n.m.r. identical with an authentic specimen).

(*l*) Ethoxy-2-*p*-methoxyphenylacetic acid (1l) gave *p*-methoxybenzaldehyde (9) and the diethyl acetal of anisaldehyde (10) (i.r. and n.m.r. identical with an authentic specimen).

(*m*) Ethoxy-*p*-tolylacetic acid (1m) gave *p*-tolualdehyde (9) and the diethyl acetal of tolualdehyde (10) (i.r. and n.m.r. identical with an authentic specimen).

(*n*) Ethoxy-2-*p*-nitrophenylacetic acid (1n) in benzene as solvent gave *p*-nitrobenzaldehyde (9), the diethyl acetal of *p*-nitrobenzaldehyde (10), and starting material (i.r. and n.m.r. identical with an authentic specimen).

(*o*) Ethoxy(trichloromethyl)acetic acid (1o) gave after separation (prep. t.l.c.) and distillation *ethoxy(trichloromethyl)methyl ethoxy(trichloromethyl)acetate* (6o), b.p. 85—90 °C/0.15 mmHg; $\nu_{max.}$ (film) 1 760 cm^{-1}; $\delta(CCl_4)$ 1.32 (6 H, t, *J* 6.8 Hz), 3.88 (4 H, q, *J* 6.8 Hz), 4.43 (1 H, s), and 6.13 (1 H, s) (Found: C, 27.3; H, 3.0. $C_9H_{12}Cl_6O_4$ requires C, 27.2; H, 3.0%).

(*p*) t-Butoxyacetic acid (1p) gave a mixture which was separated (prep. t.l.c.) and distilled to give *t-butoxymethyl t-butoxyacetate* (6p), b.p. 85—87 °C/0.15 mmHg; $\nu_{max.}$ (film) 1 760 cm^{-1}; $\delta(CDCl_3)$ 1.2 (9 H, s), 1.24 (9 H, s), 3.88 (2 H, s), and 5.33 (2 H, s) (Found: C, 60.0; H, 9.7. $C_{11}H_{22}O_4$ requires C, 60.5; H, 10.1%).

(*q*) Phenoxyacetic acid (1q) gave *phenoxymethyl phenoxyacetate* (6q), b.p. 180 °C/0.25 mmHg; $\nu_{max.}$ (film) 1 780 cm^{-1}; $\delta(CCl_4)$ 4.55 (2 H, s), 5.78 (2 H, s), and 7.0 (10 H, m) (Found: C, 69.2; H, 5.3. $C_{15}H_{14}O_4$ requires C, 69.7; H, 5.5%).

Reaction of Mercury(II) *Ethoxyacetate and Iodine.*—Mercury(II) ethoxyacetate (0.6 g, 1.4×10^{-3} mol) and iodine (0.4 g, 1.6×10^{-3} mol) were stirred in the dark in carbon tetrachloride (100 ml) for 30 min. An aliquot was withdrawn and worked up as before to give starting material (i.r.). The mixture was irradiated for 10 min. Work-up in the usual manner gave ethoxyacetic acid (0.07 g, 60%) and *ethoxymethyl ethoxyacetate* (0.13 g, 30%) (i.r., n.m.r.).

Reaction of Mercury(II) *Benzyloxyacetate and Iodine.*—Reaction of mercury(II) benzyloxyacetate with iodine as above gave, after irradiation, benzyloxymethyl benzyloxyacetate (0.3 g, 58%) and benzyloxyacetic acid (0.08, 27%).

Reaction of Benzyloxyacetic Acid with 'I_2O'.—Mercury(II) oxide (3.9 g, 1.8×10^{-2} mol) and iodine (13.7 g, 5.4×10^{-2} mol) were shaken together in benzene (75 ml) for 2 min in the dark. The mixture was filtered, treated with benzyloxyacetic acid (1 g, 6×10^{-3} mol) and irradiated for 7 h. The reaction mixture was separated into benzyl benzyloxyacetate (0.1 g) and benzyloxyacetic acid (0.45 g), identical (i.r. and n.m.r.) with authentic specimens.

Irradiation of Benzyloxyacetic Acid in the Presence of Potassium t-Butoxide and Iodine Monochloride.—Benzyloxyacetic acid (1 g, 6×10^{-3} mol) was added to a stirred mixture of iodine monochloride (5.9×10^{-2} mol) and potassium t-butoxide (6.6×10^{-2} mol) in carbon tetrachloride (100 ml) in the dark; stirring was continued for a further 15 min, and the mixture then irradiated for 3 h at 18 °C. The reaction mixture was washed (aq. sodium hydrogen carbonate–sodium thiosulphate), dried (Na_2SO_4) and concentrated to an oil (0.9 g). The major product was the benzyl t-butyl acetal of formaldehyde (70%), $\delta(CDCl_3)$ 1.22 (9 H, s), 4.52 (2 H, s), 4.75 (2 H, s), and 7.22 (5 H, s), with a trace amount of benzyloxymethyl benzyloxyacetate.

Irradiation of Isopropoxyacetic Acid with Potassium t-Butoxide and Iodine Monochloride.—Isopropoxyacetic acid (1d) was treated as above. Work-up afforded the t-butyl isopropyl acetal of formaldehyde as an oil (0.7 g), $\nu_{max.}$ (film) 3 000 cm^{-1}; $\delta(CCl_4)$ 1.11 (6 H, d, *J* 6.6 Hz), 1.2 (9 H, s), 3.8 (1 H, septet, *J* 6.6 Hz), and 4.65 (2 H, s).

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