445. *Photochemical Transformations. Part XVII.* Improved Methods for the Decarboxylation of Acids*

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The photochemical decarboxylation of acyl hypoiodites has been investigated and shown to provide an efficient method for the preparation of the corresponding nor-iodides. Primary and secondary carboxylic acids are readily decarboxylated by using the lead tetra-acetate–iodine reagent. The recently discovered t-butyl hypoiodite has been shown to form acyl hypoiodites at room temperature. With this reagent primary, secondary, and tertiary acids, as well as the hitherto intractable glutaric and adipic acids, can be decarboxylated without difficulty.

Some aspects of our work have already been reported in preliminary form.[1]

THE Hunsdiecker method for the decarboxylation of acids is well known.[2] It suffers from certain disadvantages amongst which the difficulty and expense of preparing dry silver salts may be mentioned. Recently Cristol *et al.*[3] introduced a modified Hunsdiecker procedure, using mercuric salts, which has certain advantages. At the initiation of our own work we argued that if acyl hypoiodites [4] could be prepared conveniently they might well be induced to decompose photochemically at relatively low temperatures into iodide and carbon dioxide. The important discovery of Wettstein and his collaborators [5] that the hypoiodites from alcohols can be prepared advantageously by the *in situ* interaction of lead tetra-acetate, alcohol, and iodine suggested that acyl hypoiodites might be obtained similarly.[6] Our experiments soon provided evidence that this was correct and that in many cases decarboxylation proceeded smoothly on illumination with a tungsten lamp. All the

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* Part XVI, *J.*, 1964, 2518.

[1] D. H. R. Barton and E. P. Serebryakov, *Proc. Chem. Soc.*, 1962, 309.

[2] See R. G. Johnson and R. K. Ingham, *Chem. Rev.*, 1956, **56**, 219; C. V. Wilson, *Org. Reactions*, 1957, **9**, 332.

[3] S. J. Cristol and W. C. Firth, *J. Org. Chem.*, 1961, **26**, 280; S. J. Cristol, J. R. Douglass, W. C. Firth, and R. E. Krall, *ibid.*, 1962, **27**, 2711.

[4] S.-J. Yeh and R. M. Noyes, *J. Org. Chem.*, 1962, **27**, 2978.

[5] C. Meystre, K. Heusler, J. Kalvoda, P. Wieland, G. Anner, and A. Wettstein, *Experientia*, 1961, **17**, 475; *Helv. Chim. Acta*, 1962, **45**, 1317.

[6] Cf. G. B. Bachman and J. W. Wittmann, *J. Org. Chem.*, 1963, **28**, 65.

experiments described in the present Paper were carried out with this light source. The same reactions have been studied also in the dark but the yields are inferior, the products less clear, and the rates of reaction slower.

Lead tetra-acetate itself reacts with iodine on illumination approximately according to the equation $Pb(OAc)_4 + I_2 \longrightarrow Pb(OAc)_2 + 2MeI + 2CO_2$. However, when another acid is added this is decarboxylated preferentially. The reason for this is clear from experiments recorded later in the Paper where we show that acetyl hypoiodite is stable relative to other acyl hypoiodites of the aliphatic or alicyclic series. The decarboxylation of a carboxylic acid $R{\cdot}CO_2H$ by the lead tetra-acetate–iodine reagent presumably depends upon equilibria of the following type:

$$Pb(OAc)_4 + R{\cdot}CO_2H \rightleftharpoons Pb(OAc)_3(O{\cdot}COR) + AcOH$$

$$Pb(OAc)_3(O{\cdot}COR) + I_2 \rightleftharpoons Pb(OAc)_3I + R{\cdot}CO{\cdot}O{\cdot}I$$

$$Pb(OAc)_4 + I_2 \rightleftharpoons Pb(OAc)_3I + AcOI$$

$$R{\cdot}CO_2H + AcOI \rightleftharpoons R{\cdot}CO{\cdot}O{\cdot}I + AcOH.$$

Be this as it may, the mixed reagent provides a convenient and efficient method for the decarboxylation of the illustrative range of primary and secondary carboxylic acids set out in Table 1. The reaction is most conveniently effected by adding iodine to the illuminated solution of acid and lead tetra-acetate in an inert solvent under reflux until the iodine colour persists (approx. one mol.).

The following special comments need to be made. The yield of carbon dioxide is in the range 110—130%, exceeding the theoretical because of some decarboxylation of acetyl hypoiodite. 12-Oxostearic acid was especially suited for investigation since it afforded the nicely crystalline 17-iodoheptadecane-7-one. The latter gave the known heptadecan-7-one on reduction with zinc dust in acetic acid. The constitution of the iodo-ketone was further confirmed by the fact that it had only one *C*-Me group (Kuhn–Roth) as compared with two such groups in the reduction product heptadecan-7-one. The photochemical decarboxylation of 12-oxtostearic acid was also studied by using mercuric acetate–iodine[3] and silver acetate–iodine. Although the lead tetra-acetate–iodine reagent is not remarkably superior in respect to yield it is, of course, more economic.

TABLE 1

	Molar ratios (relative to carboxylic acid)				
Acid decarboxylated	$Pb(OAc)_4$, or other oxidant	Iodine	Conditions	Yield of iodide (%)	Recovered acid (%)
n-Hexanoic	1	1·28	CCl_4, reflux	100	0
12-Acetoxystearic	1	1	CCl_4, reflux	82	—
12-Oxostearic	1·6	4·0	CCl_4, reflux	79	3
,,	1·5	2·0	CCl_4 at 10°, 84 hr.	24	53
,,	1·54	5·7	C_6H_6, reflux	87	6
,,	3·2 [$Hg(OAc)_2$]	7·0	C_6H_6, reflux	73	—
,,	3·2 ($AgOAc$)	3·6	C_6H_6, reflux	80	6
6-Benzamidohexanoic	1	1	CCl_4, reflux	63	—
Cyclohexanecarboxylic	1	1	CCl_4, reflux	91	—
Pivalic	1	1	CCl_4 at 40°, 18 hr.	10 *	40
Glutaric	2	2	CCl_4, reflux	12	55
Adipic	2	2	CCl_4, reflux	33	15

* Isobutene (20%) was also formed.

The decarboxylation of 3β-acetoxy-11-oxobisnorallocholanic acid proceeded smoothly (85%) to give a product which we at first regarded[1] as 3β-acetoxy-20α-iodoallopregnan-11-one. However, further investigations, carried out in collaboration with Dr. I. R. Puskas, showed that the product was a difficultly separable mixture of two (20α- and 20β-)iodo-compounds in approximately equal amount. Reduction of the mixed iodides with zinc dust and acetic acid gave 3β-acetoxyallopregnan-11-one, whilst treatment with aqueous acetone containing potassium carbonate followed by vigorous Wolff–Kishner reduction and then oxidation with chromium trioxide afforded allopregnane-3,20-dione. The constitutions are, therefore, established, but we have not assigned specific C-20 configurations to the two compounds.

The lead tetra-acetate–iodine reagent did not decarboxylate pivalic acid as well as hoped, whilst its behaviour with glutaric and adipic acids was disappointing. The two latter acids are notoriously difficult to degrade by the Hunsdiecker procedure.[2] In the present procedure the difficulty may have been one of solubility. However, before we could investigate this possibility further, an alternative, and superior, reagent had been devised.

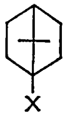
It was recently reported [7] that t-butyl hypoiodite could be prepared from the interaction of potassium t-butoxide and iodine in an inert solvent, suitably benzene. We expected that this powerful oxidising agent would undergo the following exchange reaction with carboxylic acids:

$$-\!\!|\!\!-O-I + R\cdot CO_2H \rightleftharpoons -\!\!|\!\!-OH + R\cdot CO\cdot O\cdot I$$

It should, therefore, provide a particularly convenient reagent for the photochemical decarboxylation of acids. The data summarised in Table 2 confirm this hypothesis. In general, a carboxylic acid illuminated at room temperature in benzene with t-butyl hypoiodite affords a high yield of carbon dioxide and a good yield of the corresponding iodide. Manipulative losses of iodides probably explain in part why the yields of iodide and of carbon dioxide are not identical. In the case of 12-oxostearic acid, where the derived iodide is not volatile, the two figures were essentially identical.

TABLE 2

Acid decarboxylated	Temp.	Yield (%) Iodide	Yield (%) CO_2	Recovered acid (%)
Acetic	20°	10	33	—
,,	Reflux	20	44	—
Propionic	20	26	61	—
,,	Reflux	—	76	—
n-Hexanoic	20	—	91	—
12-Oxostearic	20	78	80	5
Cyclohexanecarboxylic	20	70	90	0
Pivalic	20	—	69	—
Apocamphanecarboxylic	20	62	85	3



(I)

The t-butyl hypoiodite reagent decarboxylates tertiary acids as readily as primary or secondary acids. In particular apocamphanecarboxylic acid (I; $X = CO_2H$) gave the corresponding iodide (I; $X = I$) without any difficulty.

The t-butyl hypoiodite reagent is reasonably stable and loses little of its activity on illumination for 30 min. at room temperature (see Experimental section). It is also relatively inert towards the ethylenic linkage, at least so far as the rather reactive double bond of cholesteryl acetate is concerned. It does, however, attack alcohols rapidly.[7]

t-Butyl hypoiodite decarboxylated glutaric and adipic acids more effectively (see Table 3) than any reagent hitherto described.[2,3] In benzene adipic acid still gave an indifferent result. The difficulty, which was one of solubility, was, however, overcome by the addition of a relatively small amount of " sulpholan " (tetramethylene sulphone). The t-butyl hypoiodite reagent was destroyed by dimethyl sulphoxide and by pyridine which, otherwise, would have had suitable solvent properties. Dimethylformamide, in small amount, was useful with easily decarboxylated acids like cyclohexanecarboxylic acid, but failed with the dicarboxylic acids. More than the theoretical amount of carbon dioxide was evolved when using this solvent.

All the results reported in this Paper are explained by the simple hypothesis that the

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[7] M. Akhtar and D. H. R. Barton, *J. Amer. Chem. Soc.*, 1964, **86**, 1528.

TABLE 3

Dicarboxylic acid	Temp.	Solvent	Yield (%)		Recovered acid (%)
			CO_2	Iodide	
Glutaric	20°	C_6H_6	63	49	20
,, ...	Reflux	C_6H_6–sulpholan	85	69	0
Adipic	20	C_6H_6	18	8	75
,, ...	Reflux	C_6H_6	—	15	60
,, ...	Reflux	C_6H_6–sulpholan	80	62	0

photolysis of acyl hypoiodites affords acyloxy-radicals and iodine atoms. The loss of carbon dioxide from the former gives the corresponding carbon radicals, easily captured by the iodine present. The facile decarboxylation of apocamphanecarboxylic acid (I; $X = CO_2H$) to the corresponding bridgehead iodide (I; $X = I$) proves that radicals, and not carbonium ions, are involved.

We have also studied the decarboxylation of 1,2-dicarboxylic acids using t-butyl hypoiodite. The interesting results obtained will be reported later when further investigations have been completed.

EXPERIMENTAL

Melting points were taken on a Kofler block. Unless specified to the contrary $[\alpha]_D$ are in $CHCl_3$, ultraviolet spectra in ethanol, and infrared spectra in Nujol. Gas–liquid chromatograms were run on a Pye Argon apparatus using, unless stated otherwise, a poly(ethyleneglycol adipate) column.

Interaction of Lead Tetra-acetate and Iodine.—Lead tetra-acetate (dry; 1·33 g.) in carbon tetrachloride (25 ml.) was heated under reflux in a stream of nitrogen with irradiation from a 300 w tungsten lamp. The gas stream was passed through a trap at −80° and then through saturated aqueous barium hydroxide. Iodine (1·42 g.) in carbon tetrachloride (100 ml.) was added slowly until the iodine colour was no longer discharged (47 ml. uptake, 96% of 1 mol.). The methyl iodide was slowly distilled off into the cold trap until the b. p. was constant (pure carbon tetrachloride). Gas–liquid chromatographic analysis showed 66% of 2 mol. of methyl iodide. The yield of barium carbonate (gravimetric) was 94% of 2 mol. Filtration of the residual carbon tetrachloride gave lead diacetate (100% of 1 mol.) (infrared spectrum).

Decarboxylation of 12-*Acetoxystearic Acid with Lead Tetra-acetate and Iodine.*—The acid (6·55 g.) and lead tetra-acetate (dry; 8·58 g.) in carbon tetrachloride (25 ml.) was irradiated with a 300 w tungsten lamp and heated under reflux in a slow stream of dry oxygen-free nitrogen. Iodine (5 g.) in carbon tetrachloride (saturated solution) was added until the iodine colour was no longer discharged. The lead diacetate was removed by filtration and the solution washed with aqueous sodium thiosulphate and with water. Chromatography of the product over alumina (Grade I) gave, on elution with light petroleum (b. p. 40—60°) and with benzene–light petroleum (b. p. 40—60°) (1 : 1), 11-*acetoxy*-1-*iodoheptadecane*. This (5·95 g.) had b. p. 173—176°/1·5 mm., n_D^{24} 1·4782 (Found: C, 54·1; H, 8·75; I, 31·2. $C_{19}H_{37}IO_2$ requires C, 53·75; H, 8·8; I, 30·0%).

Decarboxylation of Pivalic Acid with Lead Tetra-acetate and Iodine.—Pivalic acid (1·98 g.) and lead tetra-acetate (9·0 g.) in carbon tetrachloride (25 ml.) was irradiated with a 300 w tungsten lamp with simultaneous cooling by fan so that the internal temperature was not >40°. Iodine in carbon tetrachloride was added slowly until the colour was permanent (18 hr.). After removal of the lead diacetate by filtration the solution was carefully distilled to give t-butyl iodide (210 mg.), b. p. 65—70°/50 mm., n_D^{24} 1·4905, identified by its infrared spectrum. During the reaction a slow stream of nitrogen was passed through the solution and then into aqueous bromine. Extraction into ether, washing with aqueous sodium thiosulphate, and evaporation gave isobutene dibromide (20%) (n_D; infrared spectrum). Pivalic acid was also recovered (40%).

Decarboxylation of 3β-*Acetoxy*-11-*oxobisnorallocholanic Acid with Lead Tetra-acetate and Iodine.* (With Dr. I. R. PUSKAS).—The acid (kindly provided by Glaxo Laboratories Ltd.) (500 mg.) in carbon tetrachloride (40 ml.) containing lead tetra-acetate (554 mg.; dried and powdered) was heated under reflux in a stream of dry oxygen-free nitrogen whilst being illuminated with a 150 w tungsten lamp. Iodine (290 mg.) in carbon tetrachloride (21 ml.) was added during 10 min. and the process continued for a further 50 min. Inorganic salts were removed by filtration and the solution washed with aqueous sodium thiosulphate. The product, in ether, was filtered through a short column of alumina (Grade V). Removal of the ether gave a solid (580 mg.), $[\alpha]_D + 26°$ (*c*. 1·0). By systematic fractional crystallisation from methanol 3β-*acetoxy*-20-*iodoallopregnan*-11-*one*-I (203 mg.), needles, m. p. 156—158°, $[\alpha]_D + 54°$ (*c* 0·86), was obtained (Found: C, 56·95; H, 7·25; I, 25·95. $C_{23}H_{35}IO_3$ requires C, 56·75; H, 7·25; I, 26·1%). Fractionation of the material in the mother-liquors gave the *isomer*-II (169 mg.), m. p. 132—135°, $[\alpha]_D + 2°$ (*c* 1·10) (Found: C, 56·65; H, 7·2; I, 26·3%).

The mixed iodides (200 mg.) in acetic acid (5 ml.) were heated under reflux for 4 hr. with activated zinc dust (500 mg.). Crystallisation of the product from light petroleum (b. p. 40—60°)–ether gave 3β-acetoxyallopregnan-11-one [8] (160 mg.; crude) (m. p. and mixed m. p.).

The mixed iodides (130 mg.) in aqueous acetone (80%) containing potassium carbonate (65 mg.) were heated under reflux for 8 hr. Removal of the solvent and Wolff–Kishner reduction [9] of the product gave crystals (60 mg.), m. p. 126—133°. The latter was taken up in acetic acid (2 ml.) containing chromium trioxide (100 mg.), added in the minimum of water. Working up in the usual way and crystallisation from aqueous methanol afforded allopregnane-3,20-dione, m. p. 198—200°, $[\alpha]_D + 117°$ (*c* 0·60).

General Procedure for Decarboxylations with Lead Tetra-acetate and Iodine.—The acid (2·5—10 mmoles) and lead tetra-acetate (dried *in vacuo* over potassium hydroxide and phosphorus pentoxide; slight excess over equimolar) were heated under reflux in an inert solvent (75—100 ml.) with stirring and illumination with a 300 w tungsten lamp for 5—20 min. (equilibrium conditions). Iodine was added in small portions until the colour persisted. A stream of dry oxygen-free nitrogen was passed throughout the experiment and the evolved carbon dioxide collected in saturated aqueous barium hydroxide (gravimetric determination). Suitable solvents were carbon tetrachloride (redistilled and dried over calcium chloride) and benzene (redistilled and dried over sodium wire). When the reaction was complete the lead salts were removed by filtration and the filtrate decolourised by shaking with aqueous sodium thiosulphate. Extraction with aqueous sodium hydroxide (1N) then removed unchanged acid. Further working up in the usual way and removal of the solvent *in vacuo* gave the product. In most cases this was analysed by gas–liquid chromatography.

The case of 12-oxostearic acid needs special comment. Decarboxylation gave 17-*iodoheptadecan*-7-*one*. This crystallised from methanol as plates, m. p. 39—40° (Found: I, 33·35; *C*-Me, 3·65. $C_{17}H_{33}IO$ requires I, 33·35; *C*-Me 3·95%). The iodo-ketone (357 mg.) in glacial acetic acid (35 ml.) was heated under reflux for 3 hr. with zinc dust (2·0 g.; added portionwise). Working up in the usual way and crystallisation from aqueous methanol gave heptadecan-7-one [10] (234 mg.) as translucent plates, m. p. 39—40° depressed to 30—37° on admixture with starting material (Found: C, 80·15; H, 13·45; *C*-Me, 6·5. Calc. for $C_{17}H_{34}O$: C, 80·25; H, 13·45; *C*-Me, 5·9%).

The following compounds had constants in agreement with the literature: 5-benzamido-1-iodopentane [11] (from 6-benzamidohexanoic acid); cyclohexyl iodide [12] (from cyclohexanecarboxylic acid); 1,3-di-iodopropane and 1,4-di-iodobutane.[13] The three liquid compounds were identified by n_D and infrared spectral comparison.

General Procedure for Decarboxylations with t-Butyl Hypoiodite.—Commercial potassium t-butoxide (2·8 mmoles) suspended in benzene (15 ml.; sodium dry) was stirred in a stream of dry oxygen-free nitrogen at 20° during the addition of iodine (4·2 mmoles; dried by repeated azeotropic distillation with benzene) in benzene (50 ml.; sodium dry) over a 30 min. period. The stirring was continued for 30 min. at 20°. All operations were carried out in darkened vessels (aluminium foil wrapping).

In the meantime a dry three-neck flask, fitted with stirrer and nitrogen inlet and outlet, was rinsed for 30 min. with dry oxygen-free nitrogen. The nitrogen was then passed through a trap cooled at −80° and a second trap containing concentrated aqueous silver nitrate. Thus freed from solvent and iodine vapours the nitrogen stream was dried (concentrated sulphuric acid or silica gel and calcium chloride) and passed through a weighed soda–asbestos tube to absorb carbon dioxide as it was formed. The acid (1 mmole) in the minimum of dry benzene in the

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[8] D. H. R. Barton, M. V. George, and M. Tomoeda, *J.*, 1962, 1967.

[9] D. H. R. Barton, D. A. J. Ives, and B. R. Thomas, *J.*, 1955, 2056.

[10] F. L. Breusch and F. Baykut, *Chem. Ber.*, 1953, **86**, 684.

[11] J. v. Braun and A. Steindorff, *Ber.*, 1905, **38**, 169.

[12] N. D. Zelinsky, *Ber.*, 1901, **34**, 2801.

[13] C. S. Marvel and A. L. Tanenbaum, *J. Amer. Chem. Soc.*, 1922, **44**, 2650.

flask was treated with the reagent solution which was filtered in quickly through a sintered-glass filter (to remove potassium salts). The reaction flask was kept at 20° (water cooling) and irradiated from underneath with stirring with a 300 w tungsten lamp for 2 hr. The content of the cold trap was added to the flask and the whole solution decolourised with aqueous sodium thiosulphate. After washing with water and drying ($MgSO_4$) the iodide content of the solution was determined according to volatility.

For acetic and propionic acids (giving methyl and ethyl iodide, respectively) the benzene solution was distilled slowly through a column until the b. p. of pure benzene had been attained. Triethylamine (2 ml.) was added to the distillate and the solution heated under reflux overnight. The solvent and excess of triethylamine were removed *in vacuo* and the yields of methyl and ethyl iodide determined as the quaternary ammonium salts. No doubt the yields are minimal owing to volatilisation losses.

Cyclohexyl iodide was determined by gas–liquid chromatography after removal of the benzene *in vacuo*. 1-Iodoheptadecan-11-one was determined by weighing after crystallisation. 1-Iodo-7,7-dimethylbicyclo[2,2,1]heptane (see below) was determined by weighing.

The decarboxylation of cyclohexanecarboxylic acid in benzene containing dimethyl sulphoxide and pyridine was not successful (reagent destroyed). In benzene containing dimethylformamide more than 100% of carbon dioxide was evolved and 70% of cyclohexyl iodide was formed. In benzene–sulpholan the corresponding yields were 87 and 73%.

Stability of the Decarboxylation Reagent.—The reagent, prepared as above, was used for the decarboxylation of 12-oxostearic acid.

Time of irradiation Before addition of acid	Time of irradiation After addition of acid	Temp.	Yields (%) CO_2	Yields (%) Iodide	Recovered acid (%)
0 min.	2 hr.	20°	80	78	5
15	2	20	80	77	4
30	2	20	83	81	5
120	2	20	21	26	68
60	2	Reflux	10	8	85

1-*Iodo*-7,7-*dimethylbicyclo*[2,2,1]*heptane.*—Apocamphanecarboxylic acid,[14] treated with t-butyl hypoiodite (see above), gave 1-*iodo*-7,7-*dimethylbicyclo*[2,2,1]*heptane*. Purified by crystallisation from 90% ethanol and sublimation at 60°/12 mm., this compound had m.p. 130—132° (capillary) (Found: C, 42·75, 42·9; H, 6·05, 6·25; I, 51·65. $C_9H_{15}I$ requires C, 43·2; H, 6·05; I, 50·75%). The nuclear magnetic resonance spectrum showed a sharp singlet at τ 9·03 (two quaternary methyl groups) and a complex multiplet between τ 7·38 and 8·80 (nine protons). This iodide is very volatile and thus the yield reported in the decarboxylation is certainly too low.

Decarboxylation of αω-Dicarboxylic Acids.—(*a*) *Without sulpholan.* The decarboxylation reagent was prepared from potassium t-butoxide (5·8 mmoles) and iodine (8·7 mmoles) as described above (same amounts of benzene). The dicarboxylic acid (1 mmole) was treated with this reagent as for the monocarboxylic acids (see above).

(*b*) *With addition of sulpholan.* The dicarboxylic acid (1 mmole) in benzene (5 ml.) and sulpholan (1·25 ml.) was treated with the decarboxylation reagent as above, the irradiation being continued for 1 hr.

(*c*) *Working up procedures.* After processing as for the monocarboxylic acids the benzene was largely removed and the yield of 1,3- or 1,4-di-iodo-compound determined by gas–liquid chromatography.

(*d*) *Other solvents.* Dimethylformamide and pyridine in place of sulpholan destroyed the reagent and prevented decarboxylation of adipic acid.

Treatment of Cholesteryl Acetate with t-Butyl Hypoiodite.—(*a*) The reagent, prepared in the usual way (see above) from potassium t-butoxide (393 mg.) and iodine (1·37 g.), was added to cholesteryl acetate (531 mg.) in benzene (50 ml.), and the solution irradiated at 20° for 2 hr. Crystallisation of the product from methanol gave back cholesteryl acetate (88%).

(*b*) The experiment was repeated under reflux with irradiation for 1 hr. Chromatography of the product over alumina (Grade III), eluting with benzene–light petroleum (b. p. 40—60°), gave, after crystallisation from methanol, unchanged cholesteryl acetate (80%).

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[14] P. D. Bartlett and L. H. Knox, *J. Amer. Chem. Soc.*, 1939, **61**, 3184.

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