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HYDROSTANNOLYSIS REACTIONS—II[1]

REACTION OF PHENOLIC ESTERS WITH TRI-n-BUTYLTIN HYDRIDE

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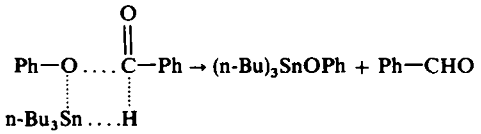
Abstract—Reaction of phenyl benzoate with tri-n-butyltin hydride has been found to give mainly toluene, benzyl benzoate, tri-n-butyltin phenoxide and tri-n-butyltin benzoate. Possible reaction paths leading to these products are discussed. A S_H2 mechanism involving initial attack of tri-n-butyltin radical at the ethereal oxygen atom of the ester with displacement of the benzoyl moiety appears to be consistent with observed experimental evidence.

Alkyl and benzylic esters have been shown to undergo hydrostannolysis to the corresponding hydrocarbons.[1] As a logical extension of this study, the reaction of tri-n-butyltin hydride with phenyl benzoate was examined. Preliminary experiments at 80° or 130° in the presence of ultraviolet light were found to give 33–37% yield of tri-n-butyltin benzoate as determined by quantitative infrared spectrophotometry. This result seemed surprising in view of the reports that aryl halides,[2] in contrast to alkyl halides, were reduced with difficulty and aryl sulphides[3] were inert to tin hydrides. Analysis of the reaction mixture by GLC however, failed to show the presence of the expected product, benzene. Diphenyl, a possible side product, was also not detected. Preparative GLC allowed the separation and identification of toluene, phenol, tetrabutyltin, unreacted phenyl benzoate and benzyl benzoate from the reaction mixture. Fractional distillation gave, after removal of low boiling products, tri-n-butyltin phenate, tri-n-butyltin benzoate and a viscous residue containing hexabutylditin and traces of metallic tin (Table 1).

Examination of the various bond dissociation energies of phenyl benzoate showed that the weakest bond in the ester is the acyl carbon-oxygen bond [$D(Ph\overset{\overset{O}{\|}}{C}—OPh) = 73$ kcal/mole *vs* $D(Ph—CO_2Ph) = 89$ kcal/mole and $D(Ph\overset{\overset{O}{\|}}{C}O—Ph) = 87$ kcal/mole respectively],[4] and thus reaction with tri-n-butyltin hydride could be expected to result in initial cleavage of this bond. Assuming bond scission indeed occurred in this manner, the formation of the various products could be accounted for by three possible mechanisms which are discussed below in the light of other experimental observations.

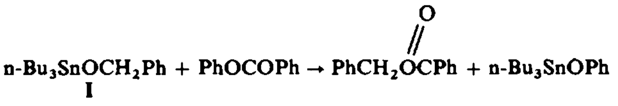
(i) *The organotin alkoxide mechanism.* The cleavage of triethyl(N-substituted formamide)tin by trialkyltin hydride in non-polar solvents has been suggested to be a four-centre type reaction.[5] Phenyl benzoate could conceivably react with tri-n-butyltin hydride in a similar manner to give tri-n-butyltin phenate and benzaldehyde [equation (1)] with the latter being converted to tri-n-butyltin benzyloxide (I) [equation (2)], since reduction of benzaldehyde by tin hydride is reported to occur also under light irradiation.[6]

Further reaction of **I** as shown by equation (3) could be envisaged



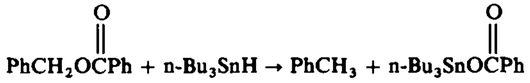
$$\begin{array}{l}\text{Ph—}\underset{\vdots}{\text{O}}\ldots\overset{\overset{\text{O}}{\|}}{\underset{\vdots}{\text{C}}}\text{—Ph} \rightarrow (n\text{-Bu})_3\text{SnOPh} + \text{Ph—CHO} \\ n\text{-Bu}_3\text{Sn}\ldots\text{H}\end{array} \qquad (1)$$

$$\text{PhCHO} + n\text{-Bu}_3\text{SnH} \rightarrow \underset{\textbf{I}}{n\text{-Bu}_3\text{SnOCH}_2\text{Ph}} \qquad (2)$$



$$\underset{\textbf{I}}{n\text{-Bu}_3\text{SnOCH}_2\text{Ph}} + \text{PhOCOPh} \rightarrow \text{PhCH}_2\text{O}\overset{\overset{\text{O}}{/\!/}}{\text{C}}\text{Ph} + n\text{-Bu}_3\text{SnOPh} \qquad (3)$$

since the Sn—O bond is known to add readily to a variety of carbonyl compounds.[7] In this work it was found that authentic **I** indeed reacted with phenyl benzoate in benzene solution at 80° to give 50% yield of benzyl benzoate. The reverse reaction, *i.e.* addition of tri-n-butyltin phenate to benzyl benzoate however, occurred only to 10% yield under identical conditions and this might be due to a difference in nucleophilicity of the oxygen atoms in tin phenate and tin alkoxide. The presence of toluene, tri-n-butyltin benzoate and phenol could arise from hydrostannolysis of the benzyl benzoate[1] [equation (4)] and tin phenate[8] [equation (5)] formed, respectively.



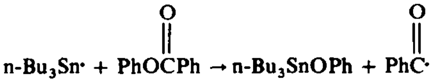
$$\text{PhCH}_2\text{O}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{Ph} + n\text{-Bu}_3\text{SnH} \rightarrow \text{PhCH}_3 + n\text{-Bu}_3\text{SnO}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{Ph} \qquad (4)$$

$$n\text{-Bu}_3\text{SnOPh} + n\text{-Bu}_3\text{SnH} \rightarrow \text{PhOH} + (n\text{-Bu}_3\text{Sn})_2 \qquad (5)$$

If the reaction occurred by the above mechanism, **I** could be expected to be present in the reaction mixture and possibly benzyl alcohol from partial hydrostannolysis of **I**.[9] Benzyl alcohol was shown to be absent from the reaction mixture by GLC and examination of the infrared spectra of distillates and residue from fractional distillation failed to show the presence of the three strong bands at 1080, 1055 and 1024 cm^{-1}, characteristic of **I**. It still remains possible that the high boiling **I** might be present in the residue in amount too small to be detected spectroscopically. Excess tri-n-butyltin hydride was therefore added to the distillation residue and after prolonged heating at 80°, benzyl alcohol was still not detected. Thus it may be deduced that the alkoxide route is probably of minor importance, if at all operative in the reaction of phenyl benzoate with tri-n-butyltin hydride.

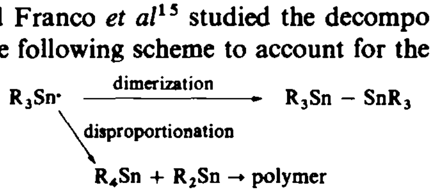
(ii) *The photo-Fries rearrangement mechanism.* Phenolic esters are known to undergo the Fries rearrangement upon irradiation. Mechanistic studies by Kobsa[10] indicated that the photo-Fries reaction of phenyl benzoate involved possibly initial homolysis into a radical pair which could either rearrange to *o*- and *p*-hydroxyaryl ketones or diffuse from the solvent cage to form polymeric radical products. In the presence of tri-n-butyltin hydride, an efficient hydrogen donor[11] however, the diffused radicals might be intercepted to form instead tri-n-butyltin phenate and benzaldehyde. The latter is known to react readily with benzoyl radicals giving the intermediate α-acyloxy radical $(\mathrm{Ph\dot{C}H{-}O\overset{\overset{O}{\|}}{C}Ph})$, which with tri-n-butyltin hydride forms benzyl benzoate[12, 13] for further hydrostannolysis accounting for the various products observed in the light-initiated reaction of phenyl benzoate with tri-n-butyltin hydride. A control experiment at 80° in the absence of tri-n-butyltin hydride, however, showed that irradiation of phenyl benzoate in cyclohexane solution with our light source, a G.E. sunlamp, gave, after 50 hr only approx 0·5% yield of *o*-hydroxybenzophenone. In contrast, irradiation with a Hanovia medium pressure light source at room temperature gave approx 10% yield of the hydroxyketone after 9 hr. These results are consistent with the observations of Kobsa[10] that only light in the region 245–330 mμ is photochemically active and radiation of longer wavelength is not sufficiently absorbed by the phenolic esters to cause Fries rearrangement. It is pertinent to mention here that when a solution of phenyl benzoate and tri-n-butyltin hydride was exposed to the medium pressure light source at room temperature for 9 hr, *o*-hydroxybenzophenone was shown to be present (6%) but benzyl benzoate could not be detected. It is plausible therefore that the products formed in the reaction of phenyl benzoate with tri-n-butyltin hydride did not arise from interception of radical intermediates due to a photo-Fries rearrangement.

(iii) *The* S_H2 *mechanism.* That the reaction of phenyl benzoate with tri-n-butyltin hydride is homolytic in nature was clearly shown by the catalytic effects various radical initiators exerted on its rate (Table 2). Attack by tri-n-butyltin radical at the ethereal oxygen with displacement of benzoyl radical [equation (6)] appears reasonable since the acyl-oxygen bond is the weakest in phenyl benzoate.[4] Subsequent reactions of the



$$\mathrm{n\text{-}Bu_3Sn\cdot + PhO\overset{\overset{O}{\|}}{C}Ph \rightarrow n\text{-}Bu_3SnOPh + Ph\overset{\overset{O}{\|}}{C}\cdot} \qquad (6)$$

benzoyl radical leading to benzyl benzoate and thence to other hydrostannolysis products are identical to those described earlier. The isolation of tin, tetrabutyltin and hexabutylditin is consistent with the presence of tri-n-butyltin radical in the reaction. Gilman and Eisch,[14] and Franco *et al*[15] studied the decomposition of triphenyltin hydride and proposed the following scheme to account for the various products:

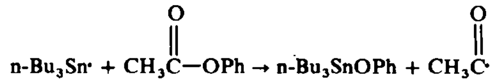


$$\mathrm{2R_2Sn \rightarrow R_4Sn + Sn}$$

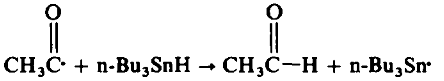
$$(\mathrm{R = Ph})$$

Tri-n-butyltin radical (R = n-Bu) might be expected to behave similarly.

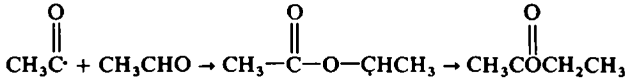
Evidence in favour of the displacement mechanism was the fact that reaction of phenyl acetate with tri-n-butyltin hydride gave as major products tri-n-butyltin phenate and ethyl acetate (Table 1). The latter was also identified by Kuivila and Walsh[13] as the main product in the hydrostannolysis of acetyl chloride and shown to arise from the reaction of acetyl radical with acetaldehyde followed by hydrogen abstraction [equation (9)], a sequence entirely analogous to that of benzoyl radical with benzaldehyde. The formation of tri-n-butyltin phenate and ethyl acetate is thus



$$\text{n-Bu}_3\text{Sn}\cdot + CH_3\overset{\overset{O}{\|}}{C}—OPh \rightarrow \text{n-Bu}_3\text{SnOPh} + CH_3\overset{\overset{O}{\|}}{C}\cdot \qquad (7)$$



$$CH_3\overset{\overset{O}{\|}}{C}\cdot + \text{n-Bu}_3\text{SnH} \rightarrow CH_3\overset{\overset{O}{\|}}{C}—H + \text{n-Bu}_3\text{Sn}\cdot \qquad (8)$$

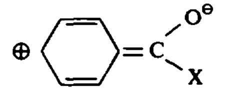


$$CH_3\overset{\overset{O}{\|}}{C}\cdot + CH_3CHO \rightarrow CH_3—\overset{\overset{O}{\|}}{C}—O—\underset{\cdot}{C}HCH_3 \rightarrow CH_3\overset{\overset{O}{\|}}{C}OCH_2CH_3 \qquad (9)$$

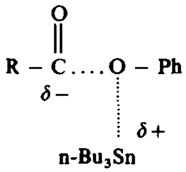
in accord with products expected from the S_H2 mechanism as represented in equations (7)–(9). The relatively poor yield of tin acetate in this case reflects the difficulty with which alkyl esters undergo cleavage by tin hydride as compared with benzylic esters.

Further evidence in support of the S_H2 mechanism was the observation that negligible reaction occurred between 2,6-dimethylphenyl benzoate and tri-n-butyltin hydride at 80° after 54 hr and only 6% reaction resulted after 48 hr at 130°. This lack of reaction could be rationalised on the basis of steric hindrance to the bulky tri-n-butyltin radical at the site of attack. Moreover, electron density at the ethereal oxygen atom seemed to influence the rate of attack of the nucleophilic tin radical[11] since a study of the relative rate of reduction showed that whereas *p*-t-butylphenyl benzoate was only half as reactive, *m*-fluorophenyl benzoate was approx 20% more reactive than phenyl benzoate towards tri-n-butyltin hydride (Table 3). Electron-withdrawing substituents on phenol appeared therefore to facilitate and electron-donating substituents to retard the reaction of tin radical at the ethereal oxygen atom.

The bond dissociation energy of the acyl carbon-oxygen bond in phenyl acetate $D(CH_3\overset{\overset{O}{\|}}{C}—OPh)$ has been calculated from available data to be approx 87 kcal,[16] which is about 14 kcal higher than the corresponding value for $D(Ph\overset{\overset{O}{\|}}{C}—OPh)$.[4] The ease with which phenyl acetate reacted with tin hydride to generate acetyl radical as shown by the extent of the reaction therefore seemed surprising. Furthermore, a competition reaction between phenyl benzoate and phenyl acetate (Table 3) also showed the latter to be approx 60% more reactive than the former. The same anomalous result was noted by Kuivila and Walsh[13] in the relative rate of hydrostannolysis of acyl halides. They reported that propionyl chloride was 5·6 times more reactive than benzoyl chloride although a study of polar effects in aroyl chlorides indicated that the reaction is facilitated by electron-withdrawing substituents. The bond dissociation energies of the C—Cl bond in acetyl chloride[17] and benzoyl chloride[18] have been estimated to be 77 kcal and 73 kcal respectively. That of propionyl chloride would be expected to be > 77 kcal and its faster rate of hydrostannolysis than benzoyl chloride has been attributed by Kuivila and Walsh[13] as possibly due to resonance contributions from such as **II** in the latter, which increase the electron density at the carbonyl group thus causing an unfavourable polar effect. Similar reasoning could be invoked for the observed relative rate of phenyl benzoate and phenyl acetate toward tri-n-butyltin hydride if the transition state of the reaction is assumed to have a substantial contribution from polar forms such as pictured in **III**.



II



$$\begin{array}{c} O \\ \| \\ R - C \ldots O - Ph \\ \delta - \quad \vdots \quad \\ \vdots\ \delta + \\ n\text{-}Bu_3Sn \end{array}$$

III

EXPERIMENTAL

M.ps and b.ps are uncorrected. IR spectra were determined on a Hilger and Watts Infrascan model 900 and UV spectra were measured with a Perkin-Elmer 137 UV spectrophotometer. GLC analyses were carried out with an Aerograph Moduline model 1520 gas chromatograph fitted with a thermal conductivity detector, employing 3 m × 2 mm column packed with either 20% SE-30, SE-52 or QF-1 on 60/80 mesh HMDS chromosorb W and using helium as carrier gas. Peak areas were determined by means of a disc integrator.

Materials

Cyclohexane used was Merck spectral grade dried over molecular sieve. Tri-n-butyltin hydride, b.p. 78–80°/0·6 mm, n_D^{26} 1·4696, lit[19] 76°/0·7 mm, n_D^{20} 1·4726, was prepared by reduction of commercial tri-n-butyltin chloride with LAH. Phenyl benzoate, m.p. 68°, and phenyl acetate, b.p. 94°/30 mm, were commercial samples, the former purified by recrystallization from EtOH and the latter by fractional distillation. *p*-t-Butylphenyl benzoate, m.p. 82°, lit[20] 81–82°, 2,6-dimethylphenyl benzoate, m.p. 41–42°, lit[21] 41–42° and *m*-fluorophenyl benzoate, m.p. 41–42° (Found; C, 72·30; H, 4·27. Calc for $C_{13}H_9O_2F$: C, 72·20; H, 4·1%) were prepared from benzoyl chloride and the appropriate phenol in pyridine and purified by column chromatography on neutral alumina.[10] Tri-n-butylbenzyloxytin, b.p. 137–138°/0·4 mm, n_D^{24} 1·5044, ν_{max} (liquid film) 1080, 1055 and 1024 cm^{-1} (Found: C, 57·01; H, 8·79; Sn, 28·77. Calc for $C_{19}H_{34}SnO$: C, 57·41, H, 8·57, Sn, 28·54%) was prepared from dibenzyl carbonate and bis(tri-n-butyltin) oxide.[22] Tri-n-butyltin phenate, b.p. 124°/0·01 mm, n_D^{26} 1·4978, ν_{max} (liquid film) 1595 cm^{-1}, lit[23] 124°/0·01 mm, was obtained from the reaction of phenol and bis (tri-n-butyltin) oxide.

General procedure

Equimolar amounts of ester and tri-n-butyltin hydride in cyclohexane (5–10 ml) were heated under N_2 at 80° and irradiated with a G.E. 275-watt sunlamp. Progress of the reaction was followed by taking aliquots at intervals and examining for the Sn-H peak at ν_{max} 1815 cm^{-1}. After completion of reaction, the mixture was analyzed quantitatively for the yields of toluene, phenol, benzyl benzoate and unreacted ester by GLC using suitable internal standards. Benzene was found to be absent, the limit of detection under the conditions employed being < 0·1 mmole. The reaction mixture was then diluted to volume with CCl_4 and the yield of tri-n-butyltin benzoate[1] determined by IR spectrophotometry at ν_{max} 1646 and 1337 cm^{-1}. After removal of solvents and volatile compds, the mixture was fractionally distilled to give (i) tri-n-butyltin phenate, b.p. 124°/0·1 mm and (ii) tri-n-butyltin benzoate, b.p. 140°/0·1 mm, identified by comparison of their IR spectra with that of authentic samples. The residue was dissolved in ether and filtered to remove metallic tin. The filtrate was shown by TLC (silica gel) to contain hexabutylditin.

TABLE 1. REACTION OF PHENOLIC ESTERS (ArOCOR) WITH TRI-n-BUTYLIN HYDRIDE[a]

ArOCOR		Initiator	Temp	Time (hr)	Unreacted ArOCOR (mmole)	Products (mmole)							
Ar	R (mmole)					RCH_3	ArOH	$ROCOCH_2R$	n-$Bu_3SnOCOR$ —SnOCOR	n-Bu_3SnOPh ArOSn—	Bu_4Sn	Sn	—Sn—Sn—
Ph	Ph (10·3)	AIBN[b]	80°	54	6·90	1·00	2·60	0·14	1·62	1·10	—[d]		—[e]
Ph	Ph (12·9)[c]	UV[b]	80°	54	8·50	1·30	1·88	0·23	1·95	2·68	—[d]		—[e]
Ph	Ph (18·9)[c]	UV	130°	46	10·50	3·90	—	0·47	4·0	3·21	—[d]	1·5	—[e]
Ph	Ph (10·3)	UV	130°	46	4·40	0·52	1·82	0·14	2·80	1·68	—[d]		—[e]
Ph	Ph (10·4)	t-Bu_2O_2[b]	130°	46	5·80	0·47	1·63	0·49	2·1	1·48	—[d]		
p-$Me_3CC_6H_4$	Ph (10·7)[c]	UV	80°	50	7·80	0·89	0·61	0·27	1·47		—[d]		—[e]
p-$Me_3CC_6H_4$	Ph (10·4)[c]	UV	130°	41	6·80	1·00	0·78	0·19	1·54		—[d]		—[e]
p-$Me_3CC_6H_4$	Ph (15·3)	UV	130°	41	7·86			0·21	3·80				
Ph	CH_3 (22·8)[c]	UV	80°	48	8·57			5·1	1·43	10·81		3·6	
2,6-$Me_2C_6H_4$	Ph (10·0)	UV	80°	52	9·6				No reaction				
2,6-$Me_2C_6H_4$	Ph (10·0)	UV	130°	50					6% reaction				

[a] Unless otherwise stated, reactions were carried out in 5–10 ml of cyclohexane (80°) or t-butylbenzene (130°).

[b] For UV, a G.E. 275-watt sunlamp was used; AIBN = azobisisobutyronitrile added was 20–30 mole % and di-t-butyl peroxide used was 2–3 mole %.

[c] No solvent was used.

[d] Detected by GLC, yield not determined.

[e] Detected by TLC (silica gel) with benzene as eluent.

TABLE 2. THE EFFECT OF RADICAL INITIATORS ON THE REACTION OF PHENYL BENZOATE WITH TRI-n-BUTYLTIN HYDRIDE

Initiator	Temp	Time (hr)	Reaction[c] %	Recovered $n\text{-}Bu_3SnH$[d] %
AIBN[a]	80°	54	33	—
UV[a]	80°	54	34	—
—[b]	80°	54	—	98
UV	130°	46	37	—
—[b]	130°	46	6	90
$t\text{-}Bu_2O_2$[a]	130°	46	40	—

[a] See footnote *a* of Table 1

[b] Uncatalyzed

[c] Based on IR spectrophotometric analysis of $n\text{-}Bu_3SnOCOPh$ (1 mole of $n\text{-}Bu_3SnOCOPh$ = 2 moles of PhOCOPh)

[d] Based on IR spectrophotometric determination of initial and final absorbances of Sn-H peak at 1815 cm^{-1}

TABLE 3. RELATIVE RATES OF REACTION OF PHENOLIC ESTERS ($R\text{-}C_6H_4OCOR$) WITH TRI-n-BUTYLTIN HYDRIDE AT 80° IN CYCLOHEXANE

R	R^1	Relative Rate
H	Ph	1
p-Me_3C	Ph	0·54 ± 0·02
m-F	Ph	1·20 ± 0·02
H	CH_3	1·55 ± 0·03

Competitive reactions

Equimolar amounts of phenyl benzoate and substituted phenyl benzoate in cyclohexane soln were allowed to compete for an insufficient amount of tri-n-butyltin hydride at 80° under irradiation with a G.E. 275-watt sunlamp for 60 hr. The unreacted esters were analyzed by GLC and the relative rate calculated according to the equation of Ingold and Shaw:[24]

$$\frac{k_B}{k_A} = \frac{\log\left(\frac{B_o}{B_f}\right)}{\log\left(\frac{A_o}{A_f}\right)}$$

where A_o and B_o are the initial amounts and A_f and B_f are the amounts of substituted phenyl benzoate and phenyl benzoate remaining after reaction respectively. Each reaction was done in duplicate or triplicate and the results averaged.

Photo-Fries rearrangement of phenyl benzoate

A soln of phenyl benzoate (1·98 g, 10 mmole) in cyclohexane (200 ml) was placed in a Hanovia photochemical reactor and irradiated at room temp with a medium pressure light source emitting predominantly at 254, 265, 297, 213 and 366 mμ. The soln was agitated by the slow passage of a stream of pure dry N_2. After 9 hr, UV spectrophotometric analysis of the reaction mixture at λ_{max} 335 mμ indicated 9% yield of *o*-hydroxybenzophenone.[25]

In a separate exp, a soln of equimolar amounts of phenyl benzoate and tri-n-butyltin hydride, when irradiated by the same light source at room temp for 9 hr, gave 6% yield of *o*-hydroxybenzophenone. No benzyl benzoate was detected by GLC.

Reaction of phenyl benzoate with tri-n-butylbenzyloxytin

A soln of phenyl benzoate (3 g, 15 mmoles) and tri-n-butylbenzyloxytin (6 g, 16 mmoles) in benzene (20 ml) was irradiated with a G.E. sunlamp at 80° for 48 hr. GLC analysis of the reaction mixture using diphenylmethane as internal standard gave recovered phenyl benzoate (6·5 mmoles) and benzyl benzoate (7·5 mmoles).

Reaction of benzyl benzoate with tri-n-butyltin phenate

A soln of tri-n-butyltin phenate (2 g, 5 mmoles) and benzyl benzoate (1·1 g, 5 mmoles) in benzene (10 ml) under identical conditions gave, by GLC analysis, phenyl benzoate (0·5 mmoles) and unreacted benzyl benzoate (4·5 mmoles).

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