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Reaction of benzoyl azide with tributyltin hydride

Benzaldehyde and benzyl benzoate were reported to be the chief products of the reaction between benzoyl chloride and organotin hydrides[1-4]. We have studied the analogous reaction of benzoyl azide with tributyltin hydride.

Reaction under reflux in hydrocarbon solvents such as petroleum ether or xylene and in the presence of azobisisobutyronitrile, gave benzamide in high yield, both in the presence of equimolar quantities of the reactants or on using two equivalents of the tributyltin hydride (Table 1). At room temperature the reaction was slow, as seen by the delay in disappearance of the characteristic bands of the Sn–H bond at 5.45 μ and of the azide bond at 4.7 μ. Here also benzamide was obtained but in lower yield (43% yield after 150 h).

TABLE 1

THE REACTION OF TRI-n-BUTYLTIN HYDRIDE WITH BENZOYL AZIDE CATALYZED BY 5 MOLE % AZOBISISOBUTYRONITRILE

$\frac{\text{Moles of hydride}}{\text{Moles of azide}}$	*Solvent*	*Temp. (°C)*	*Time (h)*	*Yield of benzamide (%)*
1	Hexane	Reflux	5	88
1	Hexane	Reflux	5	86
1	Heptane	95	5	93
2	Heptane	95	6	84
1	Isooctane	Reflux	2.5	[a]
1	Xylene	Reflux	1.5	85
2	Xylene	Reflux	1.5	91
1	Petroleum ether	68	[b]	70
2	Petroleum ether	68	[b]	79
1	Petroleum ether	Ambient	150	43

[a] The IR absorption for the azide and the Sn–H bands disappeared completely after this reaction time.
[b] The reaction was carried out for 4 h at 55°, 40 h at room temperature, followed by 2 h at 68°.

In the absence of azobisisobutyronitrile and at reflux temperatures the reaction took a much longer time. The reaction products isolated in low yield contained, besides benzamide, 1-benzoyl-3-phenylurea and 1,3-diphenylurea. It thus appears that the reaction proceeds through free radicals, as was also found in the reaction of acyl halides with organotin hydrides[1-4].

The fact that at room temperature benzamide was formed suggests that the reaction of the tributyltin hydride with benzoyl azide does not necessarily have to pass through the reactive intermediate of the Curtius rearrangement, *viz.* $C_6H_5CO\ddot{N}$:. In support of this is the fact that benzoyl azide is quite stable under these conditions[6], and the fact that the characteristic absorption band for phenyl isocyanate at 4.4 μ was not detected in a control experiment carried out without the addition of tributyltin hydride. Thus the addition of the tributyltin hydride seems to take place to the undecomposed azide molecule. On the other hand, the formation of the amide via prior formation of the intermediate $C_6H_5CO\ddot{N}$: and its subsequent reaction with the tributyltin hydride can not be excluded for the reaction carried out at high temperature.

The catalyzed reaction of the hydride with benzoyl azide, even at high temperature, appears to be faster than the rearrangement to isocyanate since no formanilide could be isolated under the existing reaction conditions. It is known that tributyltin hydride adds readily to phenyl isocyanate to give tributyl(N-phenylformamido)tin, which after hydrolysis yields formanilide[5].

We found that when the reaction was carried out in petroleum ether with rigorous exclusion of moisture, no precipitate was formed, although benzamide is insoluble in the solvent used. Addition of alcohol or water led to immediate precipitation of benzamide. Therefore it has to be assumed that the reaction leads to the formation of an organotin intermediate which is readily susceptible to hydrolysis. In fact, this intermediate was isolated by high vacuum distillation of the reaction mixture and crystallized out on cooling. It was identified as N-(tributylstannyl)-benzamide. It showed the same IR spectrum and melting point as the product obtained by reaction of bis(tributyltin)oxide with benzamide under azeotropic distillation.

The reduction of benzoyl azide with tributyltin hydride can thus be formulated as follows:

$$C_6H_5CON_3 + (C_4H_9)_3SnH \rightarrow \underset{\text{(I)}}{C_6H_5CONHSn(C_4H_9)_3} + N_2$$

$$\xrightarrow[H_2O]{\text{Hydrolysis}} C_6H_5CONH_2 + (C_4H_9)_3SnOH \ [\rightarrow (C_4H_9)_3Sn{-}O{-}Sn(C_4H_9)_3]$$

The formation of (I) may be by the following mechanism, the driving force being the evolution of nitrogen.

$$R^{\cdot}(\text{from the catalyst}) + Bu_3SnH \rightarrow RH + Bu_3Sn^{\cdot}$$

$$Bu_3Sn^{\cdot} + C_6H_5CO{-}N^{-}{-}{}^{+}N{\equiv}N \rightarrow C_6H_5CO{-}N^{\cdot}{-}SnBu_3 + N_2$$

$$C_6H_5CO{-}N^{\cdot}{-}SnBu_3 + Bu_3SnH \rightarrow C_6H_5CO{-}NH{-}SnBu_3 + Bu_3Sn^{\cdot}$$

On the other hand, in the uncatalyzed reaction the addition of the tributyltin hydride was slow and there was time for the Curtius rearrangement to take place, resulting in the formation of phenyl isocyanate. Subsequent addition of benzamide [or of N-(tributylstannyl)benzamide] present, to the phenyl isocyanate led to the formation of 1-benzoyl-3-phenylurea. Traces of water will produce aniline by reaction with phenylisocyanate and this with additional phenyl isocyanate will yield the 1,3-diphenylurea.

Experimental

Reaction of benzoyl azide with tributyltin hydride

(*a*) *In xylene, in the presence of catalyst.* To a solution of benzoyl azide (1.035 g, 7.04 mmole) and azobisisobutyronitrile (5 mole %) in xylene (50 ml), was added tri-n-butyltin hydride (4.1 g, 14.08 mmole), and the mixture was refluxed with exclusion of moisture. After 1.5 h, the reaction was complete, as seen from the disappearance of the azide absorption band in the IR spectrum. To the clear solution a few drops of methanol were added, and the crystalline precipitate formed was filtered and washed with petroleum ether, m.p. 128°, mixed m.p. and IR spectrum showed the compound to be pure benzamide. Another crop of benzamide was obtained on evaporation of the filtrate, dissolving the residual oil in petroleum ether and adding some drops of ethanol; total yield 0.78 g (91%).

(*b*) *In petroleum ether in absence of catalyst.* A solution of benzoyl azide (3.67 g, 0.025 mole) and tri-n-butyltin hydride (7.27 g, 0.025 mole) in petroleum ether b.p. 60–80° (50 ml) was refluxed for 8 h. The IR spectrum of the reaction mixture still showed strong absorption in the azide and hydride regions. The solution which contained a small crystalline precipitate was cooled, a few drops of ethanol were added, and the precipitate (2 g) was filtered and washed with petroleum ether. It was extracted twice with boiling water. The residue from the extraction was 1-phenyl-3-benzoylurea, as was evident from its m.p. (208°), mixed m.p., and IR spectrum which was superimposable on that of an authentic sample; yield 0.7 g (23%). From the extract, 0.75 g (25%) benzamide crystallized out.

(*c*) *Without solvent.* Benzoyl azide (1.47 g, 0.01 mole) and tri-n-butyltin hydride (2.91 g, 0.01 mole) were mixed without solvent and the mixture, to which azobisbutyronitrile (5 mole %) was added, was heated with exclusion of moisture at 68°. After some minutes of vigorous reaction, the mixture exploded violently, leaving a black residue.

(*d*) *N-(Tri-n-butylstannyl)benzamide.* Benzoyl azide (1.67 g, 0.011 mole), tri-n-butyltin hydride (3.3 g, 0.011 mole) and azobisisobutyronitrile (5 mole %) in petroleum ether (b.p. 60–80°) (50 ml) were heated under reflux for 2.5 h in an argon atmosphere. The resulting solution was distilled and a viscous oil passed over at 140–145°/0.001 mm, which crystallized out on cooling; m.p. 97–100°. (Found: C, 55.0; H, 8.0; N, 3.2; Sn, 30.0. $C_{19}H_{33}NOSn$ calcd.: C, 55.6; H, 8.0; N, 3.4; Sn, 29.0%.)

N-(Tributylstannyl)benzamide (3.0 g, 0.0073 mole) was dissolved in petroleum ether (100 ml), a few drops of ethanol were added and the precipitated benzamide (0.75 g, 85%) was filtered off and washed with petroleum ether. Evaporation of the filtrate left an oil, which on treatment with acetic acid gave tributyltin acetate (2.31 g, 91%).

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