$Mg^{24}$, 59.9%; $Mg^{25}$, 31.6%; and $Mg^{26}$, 8.4%; while the isotopic abundance of the magnesium-25 used was $Mg^{24}$, 0.43%; $Mg^{25}$, 99.49%; $Mg^{26}$, 0.09%. A simple calculation using this data and the natural isotope abundance for the Grignard magnesium indicates a statistical distribution of magnesium-24, -25, and -26.

## Reaction of Benzoyl Chloride with Triphenyltin Hydride

EUGENE J. KUPCHIK AND ROBERT J. KIESEL

*Department of Chemistry, St. John's University, Jamaica 32, New York*

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A recent report by Kuivila[1] on the reaction of benzoyl chloride with tri-*n*-butyltin hydride has prompted us to report our results on the reaction of benzoyl chloride with triphenyltin hydride.

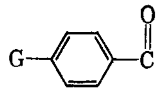
Kuivila has reported that reduction of benzoyl chloride with tri-*n*-butyltin hydride in ether gives benzaldehyde (54%) as the major reduction product; in the absence of solvent, benzyl benzoate (58%) predominates. He also has presented evidence which suggests a free-radical mechanism for this reaction. Van der Kerk, *et al.*,[2] have reported that benzaldehyde, identified as the 2,4-dinitrophenylhydrazone, and triphenyltin chloride are formed when benzoyl chloride is heated with triphenyltin hydride; no yields or detailed experimental conditions were given.

We have found that, when triphenyltin hydride and benzoyl chloride are mixed at room temperature and allowed to react at the ambient temperature, the major products formed are triphenyltin chloride and benzyl benzoate; a minor product is benzene. The results of several runs carried out under a variety of conditions are summarized in Table I. In no case could benzaldehyde be detected, either as the 2,4-dinitrophenylhydrazone, or by using gas–liquid chromatography. In a control experiment it was found that as little as 2% of benzaldehyde could be recovered as the 2,4-dinitrophenylhydrazone in 90% yield. Control experiments were always run whenever gas–liquid chromatography was employed.

The minor product of the reaction, benzene, could have originated from the benzoyl chloride or the triphenyltin hydride or from both of these compounds. Benzene has been observed as a product in several other triphenyltin hydride reactions in which it could have arisen only from the hydride.[3–5] It appears likely that it originated from the triphenyltin hydride in this case also since it was also a minor product (10% yield) of the reaction between triphenyltin hydride and *p*-methylbenzoyl chloride; no toluene was formed in this reaction, as revealed by gas–liquid chromatography. The major products were triphenyltin chloride (80.4%) and *p*-tolyl *p*-toluate (73.6%); again, no aldehyde was present as evidenced by gas–liquid chromatography and the absence of a 2,4-dinitrophenylhydrazone.

In order to determine whether the reaction of benzoyl chloride with triphenyltin hydride proceeds by an ionic or a radical mechanism it was carried out in the presence of three well-known radical inhibitors: hydroquinone,[6] *trans*-stilbene,[7] and galvinoxyl[8]; it was also carried out in the presence of azobisisobutyronitrile, a well-known radical initiator.[9] It was found that the reaction was retarded by each of the inhibitors employed and accelerated by the azobisisobutyronitrile. This result is consistent with a radical mechanism. The results are summarized in Table II.

There is an indication that electron-releasing substituents facilitate the reaction whereas electron-withdrawing substituents hinder the reaction. The results are summarized in Table III. Both electron-releasing substituents and electron-withdrawing substituents would be expected to stabilize a possible radical intermediate such as I. Our results indicate that other factors besides the stabilization of I are important in determining the rate of the reaction.



I

It should be noted that the *p*-nitrobenzoyl chloride was unreactive even in the presence of azobisisobutyronitrile. In this case the *p*-nitrobenzoyl chloride may act as its own inhibitor since nitro compounds are known to inhibit radical reactions.[10]

### Experimental

Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. Each triphenyltin hydride reaction was carried out in an atmosphere of prepurified nitrogen (Matheson). The triphenyltin chloride obtained in each reaction was identified by mixture melting point determination and infrared spectral comparison with a known sample. The acid chlorides used were all commercially available and were freshly distilled before use with the exception of *p*-nitrobenzoyl chloride which was recrystallized from *n*-hexane.

Gas–liquid chromatography data were obtained on a Perkin-Elmer vapor fractometer Model 154B. The reaction mixtures were dissolved in diethyl ether, and a 10-μl. portion of the solution was used. The per cents of benzaldehyde and benzene were determined using a diisodecyl phthalate column at 100° and a flow rate of 55 cc. of He/min. The per cents were estimated by comparison with standard chromatograms.

**Reaction of Benzoyl Chloride with Triphenyltin Hydride. A. In the Absence of Inhibitors and Accelerators.**—Triphenyltin hydride (82.0 g., 0.205 mole) and benzoyl chloride (28.9 g., 0.205 mole) were mixed at room temperature and allowed to react at the ambient temperature for 24 hr., after which time the mixture had become a thick white paste. The reaction mixture was connected to a Dry Ice–acetone trap and heated to 100° (12 mm.). In the trap was found 0.80 g. of a liquid whose infrared spectrum was superimposable on that of an authentic sample of benzene.

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(1) H. G. Kuivila in "Advances in Organometallic Chemistry," Vol. I, F. G. A. Stone and R. West, Ed., Academic Press, New York, N. Y., 1964, p. 81.

(2) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.* (London), **7**, 356 (1957).

(3) A. Stern and E. I. Becker, *J. Org. Chem.*, **27**, 4052 (1962).

(4) S. Weber and E. I. Becker, *ibid.*, **27**, 1258 (1962).

(5) F. J. Kupchik and R. J. Kiesel, *ibid.*, **29**, 764 (1964).

(6) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 431.

(7) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

(8) F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, **83**, 3461 (1961).

(9) See ref. 6, p. 70.

(10) See ref. 6, p. 168.

TABLE I

REACTION OF BENZOYL CHLORIDE WITH TRIPHENYLTIN HYDRIDE

| | | | % yield [b,c] | | |
|---|---|---|---|---|---|
| Run no. | Moles of hydride / moles of benzoyl chloride | Conditions[a] | Benzyl benzoate | Triphenyltin chloride | Benzene |
| 1 | 1 | Neat, ambient | 60.0 | 70.1 | 25[d] |
| 2 | 1 | Neat, ambient | 87.0 | 89.7 | 5 |
| 3 | 1 | Neat, ambient | *e* | 75.3 | 25[d] |
| 4 | 1 | Neat, 80° | *e* | 77.9 | *e* |
| 5 | 1 | Neat, 80° | *e* | 80.5 | 10[d] |
| 6 | 1 | Diethyl ether, reflux | 70.1 | 81.1 | *e* |
| 7[f] | 1 | Benzene, reflux | 72.4 | 81.1 | *e* |

[a] All reactions were carried out for 24 hr. [b] Unless otherwise noted, the yields are based on product isolation. [c] Using both g.l.c. and 2,4-dinitrophenylhydrazine reagent, we could not detect benzaldehyde in any of the runs in this table or when the mole ratio of hydride/benzoyl chloride was 2:1 (neat, ambient) and 5:1 (diethyl ether, reflux). [d] Estimated from g.l.c. data. [e] Not determined. [f] No benzyl alcohol was detected by g.l.c.

TABLE II

THE EFFECT OF INHIBITORS AND AZOBISISOBUTYRONITRILE ON THE REACTION OF BENZOYL CHLORIDE WITH TRIPHENYLTIN HYDRIDE[a]

| Moles of hydride / moles of benzoyl chloride | Inhibitor[b] (mole %)[c] | Time, hr. | % triphenyltin chloride[d] |
|---|---|---|---|
| 2 | (0) | 6 | 40.2 |
| 2 | Hydroquinone (3) | 6 | 0 |
| 2 | *trans*-Stilbene (50) | 6 | 0 |
| 2 | Galvinoxyl[e] (9) | 6 | 0 |
| 2 | Azobisisobutyronitrile (10) | 6 | 66.2 |
| 2 | (0) | 12 | 77.9 |
| 2 | Hydroquinone (3) | 12 | 71.3 |
| 2 | *trans*-Stilbene (50) | 12 | 0 |
| 1 | (0) | 12 | 71.4 |
| 1 | Hydroquinone (3) | 12 | 47.0 |
| 1 | *trans*-Stilbene (25) | 12 | 48.7 |
| 1 | *trans*-Stilbene (50) | 12 | 0 |
| 1 | Galvinoxyl (9) | 12 | 0 |

[a] Neat, ambient conditions. [b] Or azobisisobutyronitrile. [c] Based on moles of benzoyl chloride. [d] Based on product isolation. See footnote *b*, Table III. [e] Prepared by the method of G. M. Coppinger, *J. Am. Chem. Soc.* **79**, 501 (1957).

The residue from the distillation was extracted with three 50-ml. portions of warm diethyl ether. The ether extract was evaporated, and to the residue was added 100 ml. of petroleum ether (b.p. 30–60°). The solid material was collected on a filter to give 71.0 g. (89.7%) of triphenyltin chloride, m.p. 103–105°.

The filtrate was evaporated leaving an oil which was distilled to give 18.8 g. (87.0%) of benzyl benzoate, b.p. 114–116° (0.02 mm.); infrared spectrum was superimposable on that of an authentic sample, b.p. 114–116° (0.02 mm.).

**B. In the Presence of Azobisisobutyronitrile.**—Triphenyltin hydride (14.0 g., 0.04 mole), benzoyl chloride (2.8 g., 0.02 mole), and azobisisobutyronitrile (0.32 g., 0.002 mole) were mixed at room temperature and allowed to react at the ambient temperature for 6 hr. after which time the mixture had become a thick white paste. Petroleum ether (b.p. 30–60°, 35 ml.) was added and the reaction mixture was cooled with ice–water for 15 min. affording 7.0 g. of solid material. Further cooling at −5° for several hours gave an additional 0.5 g. of solid material. Recrystallization of the combined solids from ethanol gave 5.1 g. (66.2%) of triphenyltin chloride, m.p. 104–106°.

**Reaction of *p*-Methylbenzoyl Chloride with Triphenyltin Hydride.**—Triphenyltin hydride (21.0 g., 0.06 mole) and *p*-methylbenzoyl chloride (9.2 g., 0.06 mole) were mixed at room temperature and allowed to react at the ambient temperature for 24 hr. after which time the reaction mixture had become a thick white paste. The reaction mixture was slurried with 25 ml. of petroleum ether (b.p. 30–60°), and a 10-μl. portion of the solution was subjected to g.l.c. A peak having the same retention time as benzene was obtained. No peak having the same retention time as that for toluene was present.

The petroleum ether slurry was filtered affording a white crystalline solid which was extracted with diethyl ether. The ether extract was evaporated, and to the residue was added petroleum ether (b.p. 30–60°). The solid material was collected on a filter to give 18.5 g. (80.4%) of triphenyltin chloride, m.p. 104–106°.

TABLE III

REACTION OF *para*-SUBSTITUTED BENZOYL CHLORIDES WITH TRIPHENYLTIN HYDRIDE[a]

| *para* substituent | % yield of triphenyltin chloride[b] |
|---|---|
| $CH_3O$ | 77.9 |
| $CH_3$ | 70.1 |
| H | 32.5 |
| F | 0, 51.9[c] |
| $CF_3$ | 0, 31.1[c] |
| $NO_2$ | 0, 0[c] |

[a] Mole ratio of hydride/benzoyl chloride, 1:1; neat, ambient, 6 hr. [b] Based on product isolation of material, m.p. 103–106°. In general, petroleum ether was added to the reaction mixture which was then cooled and filtered to give the triphenyltin chloride. In cases where the tin chloride was impure, it was recrystallized from ethanol. A control experiment showed that at least 90% of the triphenyltin chloride present could be recovered by the above procedure. Addition of 2,4-dinitrophenylhydrazine reagent to the filtrate of each run failed to yield any 2,4-dinitrophenylhydrazone, indicating the absence of aldehyde. [c] Carried out in the presence of 10 mole % azobisisobutyronitrile.

The filtrate was evaporated leaving an oil which was disitlled to give 5.3 g. (73.6%) of *p*-tolyl *p*-toluate, b.p. 143–145° (0.05 mm.); infrared spectrum was superimposable on that of authentic *p*-tolyl *p*-toluate, b.p. 143–145° (0.05 mm.).