

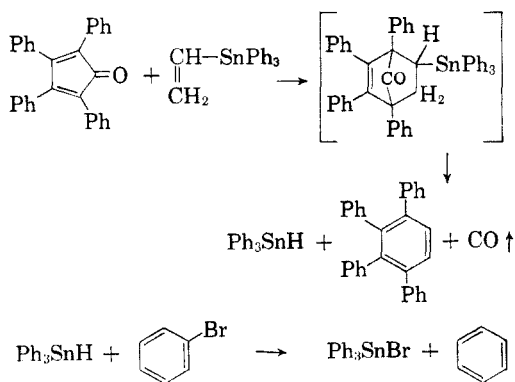
Communications TO THE EDITOR

Hydrogenolysis of Bromobenzene with Triphenyltin Hydride

Sir:

In attempting to prepare organometallic compounds *via* the Diels-Alder reaction, the reaction of tetracyclone (tetraphenylcyclopentadienone) with triphenylvinyltin in refluxing bromobenzene was examined. Among the products isolate were tetraphenyltin, m.p. 228–229° (reported:¹ 229.2°), 1,2,3,4-tetraphenylbenzene (I), m.p. 192.5–193.5° (reported:² 193–194°), 2,3,4,5-tetraphenylcyclopent-2-enone, m.p. 160–162° (reported:³ 160–162° and 162–163°), and triphenyltin bromide (II), m.p. 121.5–122.5° (reported:⁴ 121–122°)—all well-known compounds. A reducing gas was evolved throughout the course of the reaction. When tetracyclone was omitted from the boiling bromobenzene solution, tetraphenyltin was isolated, but no triphenyltin bromide.

To rationalize the appearance of these products, it was assumed that tetracyclone underwent the Diels-Alder reaction with triphenylvinyltin affording a transient adduct which eliminated carbon monoxide (the reducing gas?) and triphenyltin hydride to give fully aromatic I. The triphenyltin hydride then reacted with bromobenzene to give II and benzene.



To test this assumption a solution of triphenyltin hydride in bromobenzene was refluxed and afforded II in yields of 61–72% and benzene in yields of 60–75%.

This first example of the hydrogenolysis of an aromatic bromide with triphenyltin hydride is

(1) H. D. K. Drew and J. K. Landquist, *J. Chem. Soc.*, 1480 (1935).

(2) W. Dilthey and G. Hurtig, *Ber.*, 67B, 495 (1934).

(3) N. O. V. Sonntag, S. Linder, E. I. Becker, and P. E. Spoerri, *J. Am. Chem. Soc.*, 75, 2283 (1953).

(4) O. H. Johnson and J. R. Holum, *J. Org. Chem.*, 23, 738 (1958).

important in view of the recently reported hydrogenolyses of allyl bromide⁵ and saturated bromides.^{6,7} We have also determined that iodobenzene reacts more rapidly than bromobenzene and that chlorobenzene is least reactive.

Additional work to outline the scope of the hydrogenolysis of aromatic halogen is under way.

Acknowledgment. We are glad to thank the Metal and Thermit Corp. for the gift of generous supplies of triphenylvinyltin and triphenyltin chloride.

CHEMICAL LABORATORIES
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN 1, N. Y.

LEONARD A. ROTHMAN
ERNEST I. BECKER

Received December 8, 1958

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

(6) G. J. M. van der Kerk, J. G. A. Luijten, and J. G. Noltes, *Angew. Chem.*, 70, 298 (1958).

(7) After this Communication had been submitted, we found that J. G. Noltes and G. J. M. van der Kerk in the course of their extensive investigation of organotin chemistry independently discovered the hydrogenolysis of bromobenzene with triphenyltin hydride in 54% yield. See "Functionally Substituted Organotin Compounds," report to the Tin Research Institute, June, 1958.

A New Potent Synthetic Analgesic

Sir:

The substitution of phenethyl for methyl on the nitrogen of several well known analgesics has generally produced a marked increase in potency.¹ Well established also is the fact that one optical isomer (usually *levo*) of a racemate contains, with few exceptions, practically all of the analgesic activity.² Accordingly, we have synthesized (\pm)-2'-hydroxy-5,9-dimethyl-2-phenethyl-6,7-benzomorphan (II) and its optical isomers from (\pm)-2'-hydroxy-2,5,9-trimethyl-6,7-benzomorphan (I) (an effective analgesic in mice)³ by a route previously described.⁴ Acetylation of I with acetic anhydride gave the crude *O*-acetyl derivative

(1) J. Weijlard, P. D. Orahovats, A. P. Sullivan, Jr., G. Purdue, F. K. Heath, and K. Pfister, 3rd, *J. Am. Chem. Soc.*, 78, 2342 (1956); T. D. Perrine and N. B. Eddy, *J. Org. Chem.*, 21, 125 (1956); A. Grüssner, J. Hellerbach, and O. Schnider, *Helv. Chim. Acta*, 40, 1232 (1957); L. F. Small, N. B. Eddy, J. H. Ager, and E. L. May, *J. Org. Chem.*, 23, 1387 (1958).

(2) O. J. Braenden, N. B. Eddy, and H. Halbach, *Bull. World Health Organization*, 13, 937 (1955).

(3) This compound is comparable to morphine in analgesic effectiveness, E. L. May and E. M. Fry, *J. Org. Chem.*, 22, 1366 (1957).

(4) E. L. May, *J. Org. Chem.*, 21, 899 (1956).