Reaction of Tributyltin Enolates with α-Halogeno Ketones: a New Route to Furan Derivatives

Masanori Kosugi, Izumi Takano, Isao Hoshino, and Toshihiko Migita*
Department of Chemistry, Faculty of Technology, Gunma University, Kiryu, Gunma 376, Japan

The reaction of tributyltin enolates with α-halogeno ketones gave substituted furans which were not derived from the normal cross-coupling products, 1,4-diketones, but were formed instead through addition of the tin enolate to the α-halogeno ketones.

By analogy with the palladium-catalysed cross-coupling reaction between tributyltin enolates and various halides,[1] we expected that tributyltin enolates would react with α-halogeno ketones to form 1,4-diketones. However, a reaction took place without a catalyst to give substituted furans, which, from the substitution pattern, are not derived by the cyclization of the 1,4-diketones, but produced instead, *via* addition of the tin enolate to the α-halogeno ketone. This provides the new route to furan derivatives reported here.

The reaction of acetonyltributyltin with α-bromoacetophenone is typical. A stirred solution of acetonyltributyltin (36 mmol) and α-bromoacetophenone (20 mmol) in toluene (10 ml) was heated under argon at 80 °C for 20 h. The mixture was then washed with aqueous potassium fluoride to remove

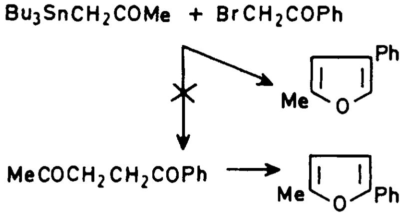
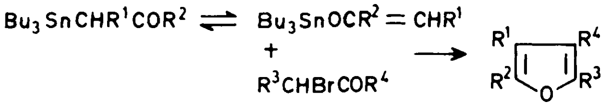


Table 1. Preparation of the furan derivatives.

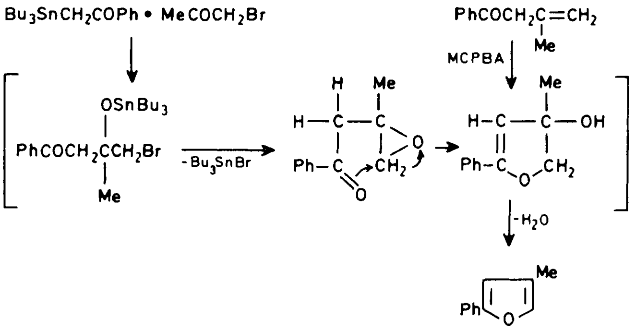


R^1	R^2	R^3	R^4	Yield (%)[a]	B.p., t/°C (p/mmHg)
H	Me	H	Ph	32	(M.p. 70—70.5)
H	Me	Me	Ph	57	112 (17)
Me	Me	H	Ph	72	128 (18)
Me	Me	Me	Ph	92	130 (13)
H	Pr	Me	Ph	80	131 (18)
$-[CH_2]_4-$		H	Ph	30	105 (0.4)
$-[CH_2]_4-$		Me	Ph	55	106 (0.2)
H	Ph	H	Me	37	(M.p. 40—41[b])
Me	Ph	H	Me	44	—

[a] Isolated yield based on halogeno ketone. [b] Y. F. Perveev, L. Shilnikova, and V. S. Gorchav, *J. Org. Chem., USSR (Eng. Transl.)*, 1972, **8**, 2286, 2288, give m.p. 39—40 °C.

the tributyltin bromide formed, and an ethereal solution of the organic layer was dried (Na_2SO_4). After evaporation, column chromatography of the residue (silica gel; cyclohexane followed by ether as eluants) provided 2-methyl-4-phenylfuran† in 32% yield.

Other furan derivatives were prepared similarly from α-bromo ketones and tributyltin enolates (Table 1), and were identified by their ^1H n.m.r. spectra. Higher yields tended to be obtained with the more substituted furans.



Scheme 1

The reaction may be explained in terms of an initial addition of enolate to the carbonyl group of the α-bromo ketone,[2] followed by elimination of tributyltin bromide to produce the β,γ-epoxy ketone,[3] which then undergoes cyclodehydration. This mechanism was supported by the fact that heating a solution of epoxidized 2-methylallyl phenyl ketone with *m*-chloroperbenzoic acid (MCPBA) gave 2-phenyl-4-methylfuran (Scheme 1).

There are a number of methods for the preparation of furan rings,[4] and the present has the advantages of simplicity and lack of additives.

Received, 7th June 1983; Com. 743

References

1 M. Kosugi, M. Suzuki, I. Hagiwara, K. Goto, K. Saitoh, and T. Migita, *Chem. Lett.*, 1982, 939; M. Kosugi, I. Hagiwara, T. Sumiya, and T. Migita, *J. Chem. Soc., Chem. Commun.*, 1983, 344.

2 J. G. Noltes, H. M. J. C. Creemers, and G. J. M. Van Der Kerk, *J. Organometal. Chem.*, 1968, **11**, 21.

3 B. Delmond and J. C. Pommier, *Tetrahedron Lett.*, 1968, 6147.

4 R. M. Acheson, 'An Introduction to the Chemistry of Heterocyclic Compounds,' Wiley, New York, 1976, pp. 149—150; T. Mukaiyama, H. Ishihara, and K. Inomata, *Chem. Lett.*, 1975, 527; M. Ishiguro, N. Ikeda, and H. Yamamoto, *ibid.*, 1982, 1029.

---

† ^1H N.m.r.: δ 7.46 (1H, s, 5-H), 7.27 (5H, br.s, 4-Ph), 6.2 (1H, s, 3-H), and 2.33 (3H, s, 2-Me).