anion also requires detailed kinetic data, which are being collected.[8]

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(8) The methods of Bergson[3] and our methods differ, although some of our conclusions correspond. Our conclusions concerning 1,3-asymmetric induction and intramolecularity in isomerization rest on isolation and analysis of products whose configuration and maximum rotations were independently determined. In three out of our four media, isotopic reservoirs of the same pK_a as the conjugate acid of the basic catalyst were present. In two of our media, both directions of isotopic exchange between substrate and media were examined. The conclusions of Bergson, *et al.*, were drawn solely from kinetic data which involved isolation of neither starting material nor product. Their elegant observation of high 1,3-asymmetric induction and its steric direction[3e] and all of their observations of intramolecularity[3] were made in the absence of isotopic reservoirs of the same pK_a as the conjugate acid of the basic catalyst. Their earlier conclusion of *high* 1,3-asymmetric induction[3d] rested on unsupported assumptions. Their results and conclusions conflict with ours only in one detail. We demonstrated that I gives II reversibly with an equilibrium constant of about 7 at 25°, whereas they state "tautomer (a) [our I] was completely rearranged to (b) [our II] as far as could be determined within the limits of experimental error."

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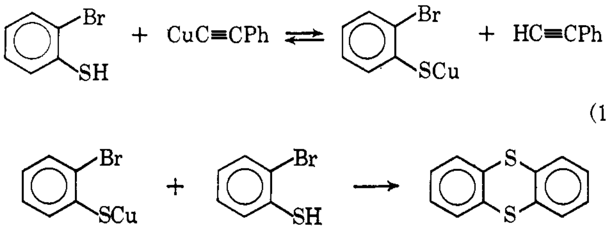
Copper(I) Substitutions. Benzo[*b*]thiophenes

Sir:

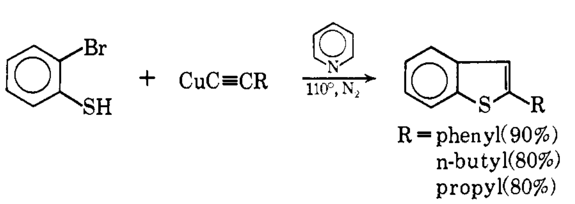
Selected benzo[*b*]thiophenes have been obtained by the pyrolysis of 2-alkylthiophenols over cupric oxide–chromic anhydride,[1] by the acid-catalyzed cyclization of aryl α-keto thioethers,[2] and *via* the reduction of 2-alkylidene-3-ketodihydrobenzothiophenes with sodium borohydride[3] and lithium aluminum hydride.[4]

We wish to report a direct one-step synthesis of 2-substituted benzo[*b*]thiophenes from *o*-bromothiophenol and cuprous acetylides. The reaction is all the more interesting because of our previous inability to obtain this heterocyclic system from these reagents.[5] Thus, reaction of a 1:1 solution of *o*-bromothiophenol and cuprous phenylacetylide in pyridine[6] yields thianthrene and phenylacetylene (1).

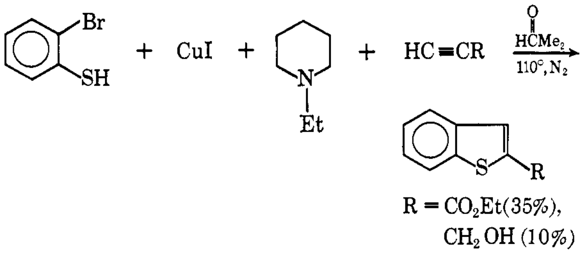


(1)

We now find that this exchange and subsequent substitutions can be circumvented by operating at high dilution of the halothiophenol. Thus, very slow (24 hr) addition of a pyridine solution of *o*-bromothiophenol to a mixture of the acetylide in pyridine affords the benzo[*b*]thiophenes in good yield. The following transformations are illustrative.[7] Less stable acetylides can be generated *in situ* (3).



(2)



(3)

These results suggest the thiophenyl moiety to be easily constructed upon a variety of aromatic systems.

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(1) C. Hansch, *et al.*, *J. Org. Chem.*, **21**, 265 (1956).

(2) J. E. Bamfield, *et al.*, *J. Chem. Soc.*, 4719 (1956).

(3) N. Kucharczyk, V. Horak, and U. Zarody, *Chem. Ind.* (London), 976 (1964).

(4) O. P. Shkurko, *Chem. Abstr.*, **63**, 11474*h* (1965).

(5) C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, **31**, 4071 (1966).

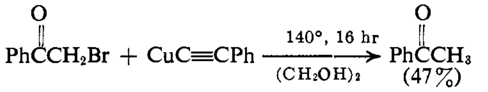
(6) The corresponding *o*-halophenols are readily converted to benzofurans under these conditions.[5]

(7) All compounds have the correct infrared, nmr, elemental analysis, and melting point where it is known. Yields represent purified substances.

Copper(I) Substitutions. Furans from α-Halo Ketones

Sir:

Unlike the lithio salt of dimethylcopper(I),[1] cuprous acetylides are not prone to react with aliphatic halides. Thus, both alkyl and benzyl bromides are inert toward cuprous acetylide under conditions that allow for an easy substitution of aryl halides.[2] Phenacyl bromide affords intractable tars upon long reflex with cuprous acetylides in dimethylformamide and is reduced to acetophenone[2] by either cuprous bromide or cuprous phenylacetylide in ethylene glycol[2] (1). At higher tem-



$$\mathrm{Ph\overset{O}{\overset{\|}{C}}CH_2Br + CuC{\equiv}CPh \xrightarrow[(CH_2OH)_2]{140^\circ,\ 16\ hr} Ph\overset{O}{\overset{\|}{C}}CH_3}\ (47\%) \qquad (1)$$

peratures, these halides can be cleanly substituted.[3] All reactions were conducted in sealed tubes under nitrogen.

$$\mathrm{PhCH_2Br + CuC{\equiv}CPh \xrightarrow[\text{N-methyl-pyrrolidone}]{245^\circ,\ 5\ min} PhCH_2C{\equiv}CPh}\ (90\%) \qquad (2)$$

$$\mathrm{CH_2{=}CHCH_2Br + CuC{\equiv}CPh \xrightarrow[PhNO_2]{240^\circ} CH_2{=}CHCH_2C{\equiv}CPh}\ (83\%) \qquad (3)$$

Most significantly, α-halo ketones can be converted in one step to the corresponding furans. The examples in eq 4–7 are illustrative.

In no case was the uncyclized acetylenic ketone isolated. Cyclization through the copper-coordinated enol[4] is consistent with the ready preparation of benzo-

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(1) E. J. Corey and G. H. Posner, *J. Am. Chem. Soc.*, **89**, 3911 (1967).

(2) C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, **31**, 4071 (1966), and references therein.

(3) The yields of all reactions reported herein do not vary appreciably with the diluents nitrobenzene, N-methylpyrrolidone, or α-methylnaphthalene. Yields are somewhat less when the reaction is conducted without solvent. The yields are given for purified substances.

(4) That is, Cu(I) (like Cu(II)) salts must catalyze the enolization; *cf.* C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, **30**, 587 (1965).