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

(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."

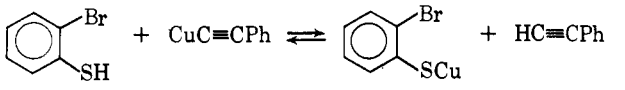
John Almy, Roy T. Uyeda, Donald J. Cram
Contribution No. 2138, Department of Chemistry
University of California, Los Angeles, California 90024
Received October 28, 1967

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

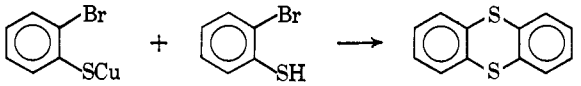
Sir:

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]

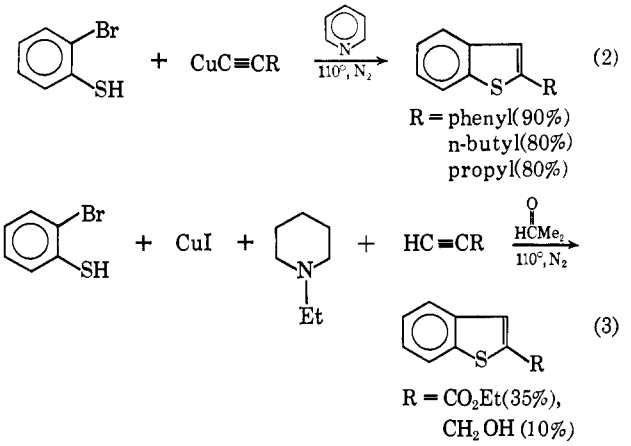
We wish to report a direct one-step synthesis of 2-substituted benzo[*b*]thiophenes from *o*-bromothiophenol and cuprous acetylides. The reaction is all the more interesting because of our previous inability to obtain this heterocyclic system from these reagents.[5] Thus, reaction of a 1:1 solution of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



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

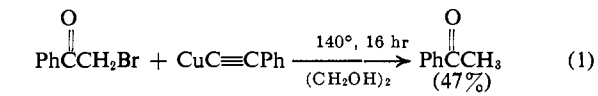
Acknowledgment. We are grateful to the National Institutes of Health (AI05132) for generous support.

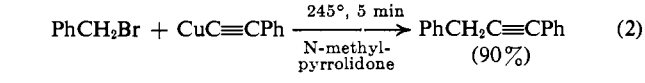
A. M. Malte, C. E. Castro
Department of Nematology, University of California
Riverside, California 92507
Received October 25, 1967

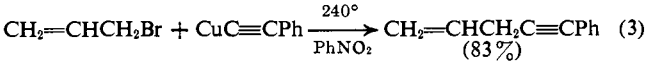
Copper(I) Substitutions. Furans from α-Halo Ketones

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





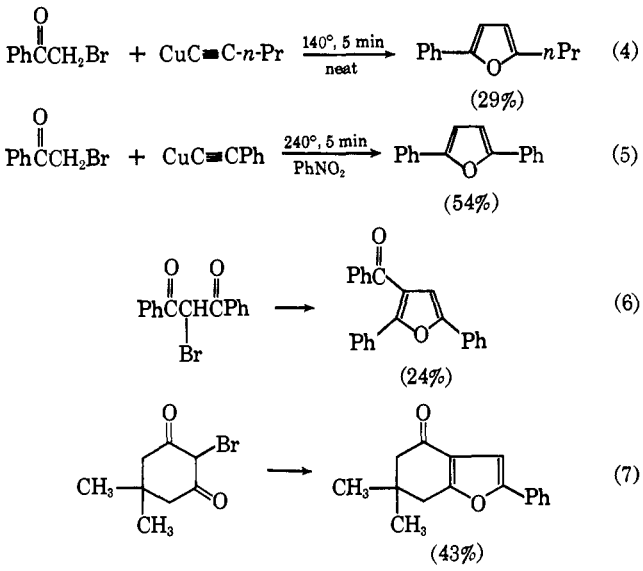


Most significantly, α-halo ketones can be converted in one step to the corresponding furans. The examples in eq 4–7 are illustrative.

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

(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.

(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).



furans[2] and benzo[*b*]thiophenes[5] from *o*-halophenols and thiophenols and with the conversion of *o*-halopyridinols (pyridones) to furopyridines.[2,6] Reactions 4–7 suggest the possibility of a synthesis of unusual heterocyclic systems from a variety of carbonyl derivatives.

Acknowledgment. The authors are grateful to the National Institutes of Health (AI04132) for generous support.

(5) A. M. Malte and C. E. Castro, *J. Am. Chem. Soc.*, 89, 6770 (1967).

(6) A general synthesis of a wide array of furo[3,2-*b*]pyridines and furo[3,2-*c*] pyridines will be reported shortly. The keto tautomer is the dominant form of "hydroxypyridines" in the solid state and in solution: "Heterocyclic Compounds, Pyridine and its Derivatives," Part 1, E. Klingsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 67.

(7) To whom inquiries should be addressed.

K. Gump, S. W. Moje, C. E. Castro[7]
Department of Nematology, University of California
Riverside, California 92507
Received October 25, 1967

Preparation and Properties of $B_5H_8^-$ Salts. A New Synthesis of Decaborane(14)

Sir:

Recent reports by Gaines and Iorns[1] and by Onak, Dunks, Searcy, and Spielman[2] on the existence of $B_5H_8^-$ prompt us to describe results of independent studies carried out in this laboratory. We have prepared a number of salts of $B_5H_8^-$, examined its boron-11 nmr spectrum, and investigated some of its reactions, including one which results in the formation of $B_{10}H_{14}$. Initial results are reported at this time.

In a procedure similar to that of Gaines and Iorns,[1] LiB_5H_8 was prepared through the reaction of methyllithium with pentaborane(9). Samples were maintained at −78° to minimize decomposition. Sodium and potassium salts of $B_5H_8^-$ were generated by allowing a metal hydride to react with an equimolar amount of pentaborane(9) in glyme at −50°. An equivalent amount of hydrogen was produced after several hours

(1) D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.*, 89, 3375 (1967).
(2) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, 6, 1465 (1967).

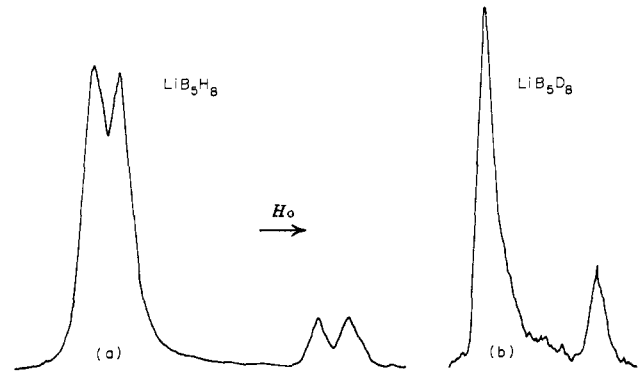


Figure 1. (a) The ^{11}B nmr spectrum (32.1 Mc) of LiB_5H_8 at 35°. Chemical shifts (ppm from $BF_3 \cdot O(C_2H_5)_2$) and coupling constants (cps in parentheses) are 17.0 (127) and 52.7 (156). (b) The ^{11}B nmr spectrum (19.3 Mc) of LB_5D_8 at 23°. Chemical shifts (ppm from $BF_3 \cdot O(C_2H_5)_2$) are 17.8 and 53.7.

at this temperature. Onak and co-workers[2] obtained

$$MH + B_5H_9 \xrightarrow{\text{glyme}} H_2 + MB_5H_8(\text{solvate})$$
$$M = Na, K$$

equivalent amounts of hydrogen in analogous reactions, which were carried out at room temperature. However, it seems clear from the present investigation that the nmr spectrum they report for the $B_5H_8^-$ ion is more likely that of a decomposition or rearrangement product. We have found that the sodium and potassium salts of $B_5H_8^-$ decompose rapidly in glyme on approaching room temperature; a light yellow precipitate appears and the high-field doublet in the boron-11 nmr spectrum disappears. On the other hand, samples of LiB_5H_8 in solution show no apparent decomposition for periods of up to 1 hr at room temperature.

Boron-11 nmr spectra of LiB_5H_8, NaB_5H_8, and KB_5H_8, generated and kept at low temperature to prevent decomposition, are simpler than those previously reported.[1,2] They consist of an upfield doublet, assigned to an apical boron, and a low-field doublet, assigned to basal borons. The chemical shift and coupling constant of the high-field doublet are essentially constant over the temperature range −80–35°. However, the low-field doublet in the LiB_5H_8 spectrum is temperature dependent. The chemical shift goes to higher field, and the coupling constant decreases with increasing temperature. From −80 to −60°, the low-field doublet is symmetrical in appearance; from −50 to 0°, it is asymmetric in appearance, resolving to a symmetrical doublet at room temperature (Figure 1a). Asymmetry of the low-field doublet at low temperature is consistent with the earlier report,[1] but in none of the spectra of undecomposed $B_5H_8^-$ salts, over the entire temperature range studied, was a peak at 11.8 ppm observed. This peak might arise from unreacted pentaborane(9) or from decomposition of the specimen.

The boron-11 nmr spectrum of LiB_5D_8 at room temperature is presented in Figure 1b. Two symmetrical singlets, one corresponding to an apical boron and one corresponding to apparently magnetically equivalent basal borons, were seen over the range −80 to 35° in the spectra of the deuterated species. The boron-11 nmr spectra are consistent with a pyramidal