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MERCURY IN ORGANIC CHEMISTRY

I. A CONVENIENT SYNTHESIS OF GEMINAL DIMERCURIALS FROM TERMINAL ACETYLENES

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SUMMARY

1,1-Bis(chloromercuri)alkanes are readily prepared from terminal acetylenes via hydroboration–mercuration using "borane". Attempted synthesis of these compounds utilizing disubstituted boranes has thus far failed. The physical properties of several new *gem*-dimercurials are reported.

INTRODUCTION

Relatively few organometallic compounds containing two metal atoms on the same carbon atom (*gem*-dimetallics) have been prepared. The first such compound to be synthesized, however, was obtained as early as 1881. Sakurai[1] found that methylene iodide and elemental mercury react under the influence of sunlight to give bis(iodomercuri)methane (eqn. 1). *gem*-Dimercurials can also be obtained from *gem*-diboro compounds. Thus, Matteson has converted a 1,1-ethenediboronic ester to a *gem*-dimercurial[2], and 1,1-bis(dibutoxyboryl)ethane to 1,1-bis(chloromercuri)ethane[3].

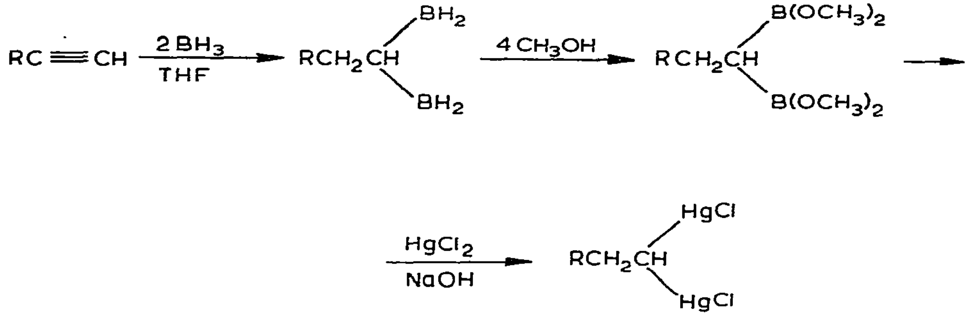
$$CH_2I_2 + 2\,Hg \rightarrow CH_2(HgI)_2 \qquad (1)$$

In view of the ready availability of a large number of *gem*-diboro compounds via hydroboration of acetylenes[4], we have investigated the possibility of converting these compounds into the corresponding *gem*-dimercurials.

RESULTS AND DISCUSSION

Mercuration of 1,1-*diboroalkanes*

We chose 1-pentyne as a representative terminal alkyne and examined its conversion into 1,1-bis(chloromercuri)pentane (eqn. 2). The acetylene was hydroborated by adding either 2 equivalents of "borane" to the acetylene or the acetylene to the "borane" in sufficient cold tetrahydrofuran (THF) ($0°$) to obtain a 0.5 *M* solution of diboroalkane. Neither the mode nor the duration of the hydroboration seemed to greatly affect the yield. One hour appeared to be sufficient, at which time a clear yellow



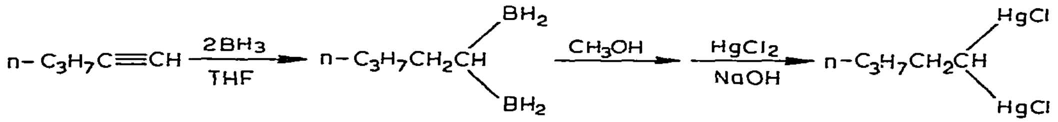
(2)

solution was present. Excess methanol was slowly added at 0° and stirred 1 h at room temperature to obtain the tetramethyl diboronate and hydrogen. Varying amounts of solid mercuric chloride and 5 *M* aqueous sodium hydroxide were added and stirred 24 h. The reaction mixture gradually changes from a rust orange color to white or pale pink over several hours time. This product was poured into 1 l of cold dilute hydrochloric acid, stirred and collected by filtration. This crude product usually contained mercurous salts which were readily removed by dissolving the dried white solid in pyridine, filtering free of metallic mercury and pouring back into a large amount of ice water. Vacuum filtration and drying gave a white solid product. The yield of *gem*-dimercurial was relatively independent of the number of equivalents of mercuric chloride used (beyond 2), but jumped sharply with an increase in the number of equivalents of sodium hydroxide. At least three equivalents of base appear necessary to obtain good yields. A maximum yield of 68 % could be realized using this procedure. The results of this study are summarized in Table 1.

The generality of this procedure was examined on several other acetylenes. 1-Hexyne, 1-decyne, 3,3-dimethyl-1-butyne and phenylethyne were chosen and the yields obtained when employing 4 equivalents of mercuric chloride and sodium

TABLE 1

PREPARATION OF 1,1-BIS(CHLOROMERCURI)PENTANE

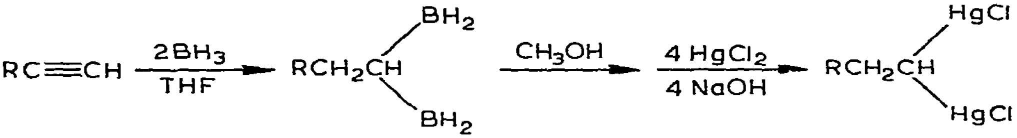


$HgCl_2$ Equivalents	*NaOH Equivalents*	*Yield[a] (%)*
2.0	2.0	34
2.0	3.0	64
2.0	4.0	67
3.0	3.0	68
4.0	2.0	40
4.0	3.0	66
4.0	4.0	65

[a] Isolated, purified yield based on acetylene.

TABLE 2

PREPARATION OF 1,1-BIS(CHLOROMERCURI)ALKANES



$$RC{\equiv}CH \xrightarrow[THF]{2BH_3} RCH_2CH(BH_2)_2 \xrightarrow{CH_3OH} \xrightarrow[4\,NaOH]{4\,HgCl_2} RCH_2CH(HgCl)_2$$

Alkyne	*Yield*[a] (%)
1-Pentyne	65
1-Hexyne	67
1-Decyne	77
3,3-Dimethyl-1-butyne	68
Phenylethyne	58

[a] Isolated purified yield based on acetylene.

hydroxide were determined. Yields of 58–77% could be obtained (Table 2). It is obvious that this procedure provides a very convenient route to compounds which would otherwise be extremely difficult to prepare. It is most likely that the major difficulty in this procedure is the hydroboration step and not the mercuration reaction. Considerable amounts of 1,2-diboroalkane are probably also obtained upon hydroboration.

Characterization of 1,1-*bis(chloromercuri)alkanes*

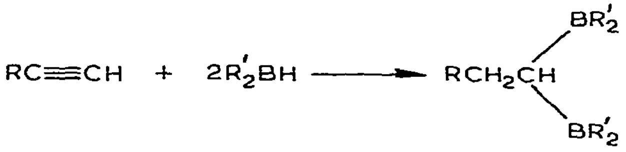
All the 1,1-bis(chloromercuri)alkanes prepared were high melting white crystalline solids. They are quite insoluble in most organic solvents, although readily soluble in highly polar aprotic solvents such as *N*,*N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), hexamethylphosphoric triamide (HMPT) as well as pyridine. They could be recrystallized very well from 95% ethanol/DMF and are readily handled in air. They appear thermally stable at least up to their melting points. All compounds gave excellent elemental analyses for carbon, hydrogen and mercury.

The NMR spectra of these compounds also proved interesting. Due to their low solubility in the standard NMR solvents, we were forced to use one of the above mentioned solvents. Pyridine proved quite useful except for the phenyl substituted compound.

The physical properties and NMR spectra of these compounds are summarized in Tables 3 and 4.

Attempted synthesis via disubstituted boranes

In an attempt to improve the yields of 1,1-bis(chloromercuri)alkanes we have examined the utilization of several other hydroborating agents. It is known that the hydroboration of terminal acetylenes with dicyclohexylborane gives excellent yields of the 1,1-diboroalkanes (eqn. 3). We have examined the possibility of converting



$$RC{\equiv}CH + 2R'_2BH \longrightarrow RCH_2CH(BR'_2)_2 \qquad (3)$$

TABLE 3

PHYSICAL CHARACTERISTICS OF 1,1-BIS(CHLOROMERCURI)ALKANES, R–CH(HgCl)$_2$

R	*M.p.*[a] *(°C)*	*Analysis, found (calcd.) (%)*		
		C	*H*	*Hg*
n-C_4H_9	135	10.84	2.14	74.21
		(11.08)	(1.86)	(73.99)
n-C_5H_{11}	153.5-154	13.05	2.00	72.12
		(12.93)	(2.17)	(71.99)
n-C_9H_{19}	[b]	19.87	3.39	65.77
		(19.61)	(3.29)	(65.51)
$(CH_3)_3CCH_2$	>250[b]	12.82	1.97	72.09
		(12.93)	(2.17)	(71.99)
$C_6H_5CH_2$	245-246	16.64	1.44	69.40
		(16.68)	(1.40)	(69.92)

[a] Recrystallized from 95% ethanol/DMF. [b] A sharp melting point was never obtained.

TABLE 4

NMR OF *1,1-BIS(CHLOROMERCURI)ALKANES*, R–CH$^2_2$–CH^1(HgCl)$_2$

Formula	*δ(H¹)* *(ppm)*	*δ(H²)* *(ppm)*	*J(H¹–H²)* *(Hz)*	*J(¹⁹⁹Hg–H¹)* *(Hz)*
n-$C_4H_9CH(HgCl)_2$	3.33	2.07	7–8	200
n-$C_5H_{11}CH(HgCl)_2$	3.28	2.08	7–8	188
n-$C_9H_{19}CH(HgCl)_2$	3.30	≈2.10	7–8	188
$(CH_3)_3CCH_2CH(HgCl)_2$	3.01	2.19	7–8	194[b]
$C_6H_5CH_2CH(HgCl)_2$	3.50[a]	3.50[a]		190[b]

[a] It is clear these are not exactly equal. [b] The assignment of satellites is uncertain.

these organoboranes into organomercurials. Mercuric chloride and acetate appeared to react with the 1,1-diboroalkane, but no recognizable product could be isolated. The use of mercury(II) alkoxides in THF gave some fascinating results. The addition of mercuric chloride and solid potassium t-butoxide to a THF solution of the 1,1-diboro derivative gave a 68% yield of cyclohexylmercuric chloride! We have recently observed that this facile reaction of mercury alkoxides with sec-alkylboranes provides a convenient route from internal olefins to sec-alkylmercuric salts[5].

Thus, all attempts to improve the yields of 1,1-bis(chloromercuri)alkanes by utilizing dicyclohexylborane have so far failed.

CONCLUSION

The hydroboration of terminal acetylenes with "borane" gives good yields of 1,1-diboroalkanes which are readily converted to 1,1-bis(chloromercuri)alkanes by treatment with methanol, mercuric chloride and sodium hydroxide in that order. Isolated purified yields of 58–77% can be obtained. All attempts to improve the yields by using other hydroborating agents have so far failed. This procedure utilizing organoboranes is the only convenient general route presently available for the synthesis of *gem*-dimercurials. These interesting new mercury compounds should prove useful intermediates for the synthesis of other *gem*-dimetallic compounds as well as other organic derivatives. We are presently exploring these possibilities.

EXPERIMENTAL

Materials

All glassware was dried thoroughly in a drying oven and cooled under a stream of nitrogen. THF was dried over lithium aluminum hydride, distilled and kept under nitrogen. The "borane"[6] and dicyclohexylborane[7], were prepared according to literature procedures. All acetylenes were used directly as obtained from Farchan. Baker "analyzed" mercuric chloride and methanol were also used directly as obtained.

All melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories. The NMR spectra were obtained on Varian A-60 and HA-100 NMR spectrometers, with pyridine used as the normal NMR solvent.

Hydroboration–mercuration of acetylenes with "borane"

A dry 250 ml flask with septum inlet was purged with dry nitrogen and filled with 30 ml of THF. After cooling the flask to 0° either the acetylene (25 mmole) or the "borane" (20 ml of 2.50 *M*) were added first to be followed by slow addition of the other reagent. After stirring for the appropriate length of time (usually 1 h) at room temperature, the flask was again cooled to 0° and 10 ml of methanol was slowly added. After 1 h at room temperature the appropriate amount of solid mercuric chloride (100 mmole for most preparative reactions) was added to the flask while backflushing with nitrogen. The appropriate amount of 5 *M* aqueous sodium hydroxide (usually 20 ml) was then added dropwise with vigorous stirring. After stirring 24 h at room temperature, the reaction mixture was poured into 1 l of dilute hydrochloric acid and stirred. The white solid was collected by filtration, washed thoroughly with water and dried. This solid was purified by dissolving in pyridine, filtering free from metallic mercury, pouring into 1 l of ice water and once again collecting and drying the compound under vacuum. All recrystallizations were readily achieved using 95% ethanol and DMF.

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REFERENCES

1 J. Sakurai, *J. Chem. Soc.*, 39 (1881) 485.
2 D. S. Matteson and P. B. Tripathy, *J. Organometal. Chem.*, 21 (1970) P6.
3 D. S. Matteson and J. G. Shdo, *J. Org. Chem.*, 29 (1964) 2742.
4 H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, 83 (1961) 3834.
5 R. C. Larock, manuscript in preparation.
6 H. C. Brown and R. L. Sharp, *J. Amer. Chem. Soc.*, 90 (1968) 2915.
7 R. C. Larock and H. C. Brown, *J. Organometal Chem.*, 36 (1972) 1.