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1-ALKENE-1,1-DIBORONIC ESTERS AND 1,1-BIS(CHLOROMERCURI)-1-ALKENES

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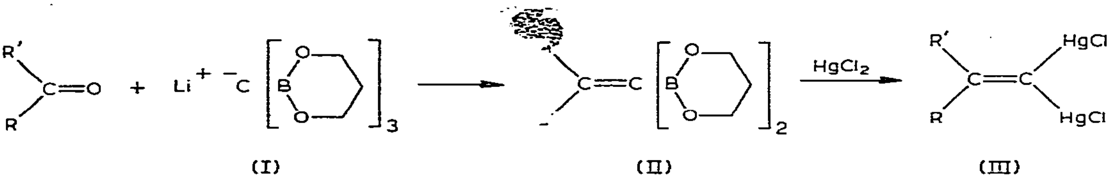
Summary

Several 1,1-bis(trimethylenedioxyboryl)-1-alkenes (II) have been prepared and converted efficiently to 1,1-bis(chloromercuri)-1-alkenes (III) by reaction with mercuric chloride and sodium acetate in aqueous methanol. Preparations of a 1,1-diiodo-1-alkene (IV) and three 1,1-bis(ethylenedioxyboryl)-1-alkenes are also described.

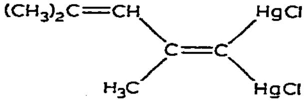
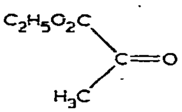
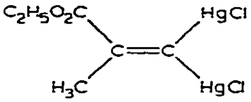
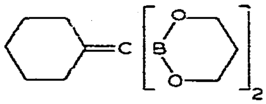
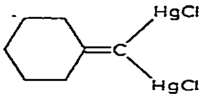
The reaction of lithium triborylmethides, $Li^{+}\,{}^{-}C[B(OR)_2]_3$, with aldehydes or ketones yields 1-alkene-1,1-diboronic esters, $RR'C{=}C[B(OR)_2]_2$, one of which has been treated with mercuric chloride and sodium acetate in aqueous methanol to precipitate the 1,1-bis(chloromercuri)-1-alkene, $(CH_3)_2C{=}C(HgCl)_2$ [1]. An improved procedure starts with lithium tris(trimethylenedioxyboryl)methide (I) and gives generally good yields of 1,1-bis(trimethylenedioxyboryl)-1-alkenes (II) [2]. In the present work, several examples of II, which need not be fully purified, have been converted in high yields to 1,1-bis(chloromercuri)-1-alkenes (III). Results are summarized in Table 1.



The 1,1-bis(chloromercuri)-1-alkenes (III) precipitated immediately on mixing the solutions of reactants at 20—25°C. Several of the precipitates were analytically pure, the others were recrystallized once from dimethylformamide and ethanol. The replacement of boron by mercury is evidently quantitative, as shown by the yield of bis(chloromercuri)methylenecyclohexane from the purified boronic ester (Table 1). In the other reactions, the boronic ester intermediates II were freed of the lithium borate by-product [2], which darkened the precipitated III if not removed, but were not purified further. The overall yields of the mercury

TABLE 1

CONVERSION OF CARBONYL COMPOUNDS BY WAY OF ALKENE-1,1-DIBORONIC ESTERS (II) TO 1,1-BIS(CHLOROMERCURI)-1-ALKENES (III)

Starting material	Product (III)	Yield (%)	Melting point (°C)
$(CH_2O)_x$	$H_2C{=}C(HgCl)_2$ [a]	70	>250
$(C_2H_5)_2CHCHO$	$(C_2H_5)_2CHCH{=}C(HgCl)_2$	81	173—175 [b]
C_6H_5CHO	$C_6H_5CH{=}C(HgCl)_2$	85	258—260 dec.
CH_3COCH_3	$(CH_3)_2C{=}C(HgCl)_2$ [c]	85	>250
$(CH_3)_2C{=}CHCOCH_3$		74	169—172
		80	204—207 [b]
		97 [d]	175—176

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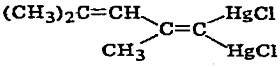
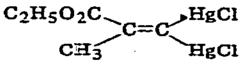
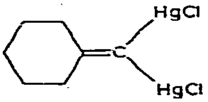
[a] This was the only product not obtained analytically pure. Note that the intermediate boron compound II requires a modified preparative procedure in this case [2]. [b] Analytical sample recrystallized from dimethylformamide/ethanol. [c] Compound reported previously [1]. [d] Corresponds to 85% based on cyclohexanone.

TABLE 2

60 MHz ^1H NMR SPECTRA OF 1,1-BIS(CHLOROMERCURI)-1-ALKENES (III) [a]

Compound	Solvent	$Hg_2C{=}C\underline{H}$—			$Hg_2C{=}C{-}C\underline{H}$—		Other	
		δ	J_{cis}	J_{trans}	δ	J_{trans} [b]	δ	Group
$H_2C{=}C(HgCl)_2$	DMSO-d_6	5.92	379	740				
$(C_2H_5)_2CH\text{-}CH{=}C(HgCl)_2$	DMSO-d_6	6.26	296	688	Not resolved		0.6—2.0	Et_2CH
$C_6H_5CH{=}C(HgCl)_2$	DMSO-d_6	7.73 [c]	336	694			7.3—8.0	C_6H_5
$(CH_3)_2C{=}C(HgCl)_2$	DMSO-d_6				2.02 [d]	36 [d]		
 $(CH_3)_2C{=}CH(CH_3)C{=}C(HgCl)_2$	Pyridine-d_5				6.34 [e] 2.26 [g]	38 38	1.64 [f] 1.90 [f]	CH_3 CH_3
 $C_2H_5O_2C(CH_3)C{=}C(HgCl)_2$	DMSO-d_6				2.56	39	1.20 [h] 4.25 [i]	CH_3 CH_2
	Pyridine-d_5				2.6 [j]		1.6	$(CH_2)_3$

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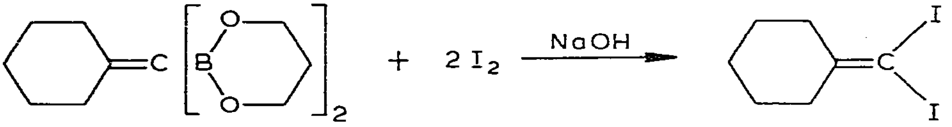
[a] δ in parts per million from TMS, J in Hz, integral values in agreement with theory. [b] Larger splitting assumed to be J_{trans}. J_{cis} may be about 5 Hz from shape of peaks at bases. [c] Overlaps C_6H_5 multiplet, calculated from satellites. [d] Same as reported previously [1]. [e] Broad singlet, =CH. [f] Singlet. [g] Singlet, CH_3. [h] Triplet. [i] Quartet. [j] Broad, satellites not detected.

compounds III from the aldehydes or ketones were the same as or up to 4% higher than those of the boronic ester intermediates II reported previously [2] in three cases, paraformaldehyde, benzaldehyde, and acetone. The remaining boronic ester intermediates II, from 3-ethylpentanal, mesityl oxide, and ethyl pyruvate, have not been made previously and were not isolated in the present work, their efficient production being sufficiently proved by the easier isolation of their mercury derivatives III.

The ^{1}H NMR spectra of the new mercury compounds III, summarized in Table 2, show ^{199}Hg satellites typical of alkenylmercury compounds [3].

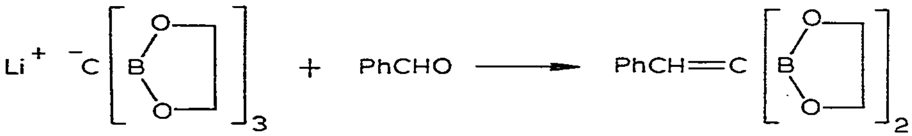
Another potentially useful electrophilic displacement of boron from alkeneboronic acids is iododeboronation to the iodoalkene [4]. Iododeboronation of bis(trimethylenedioxyboryl)methylenecyclohexane yielded 71% diiodomethylenecyclohexane (IV).



(IV)

In the foregoing and other recent work with alkene-1,1-diboronic esters [2,5], the 1,3-propanediol ester (trimethylenedioxyboryl) series was chosen as accessible and convenient. However, propanediol distributes in both the ether and the aqueous phases in reactions which require hydrolysis and extraction in the workup, and it can be a nuisance to separate, as in the oxidation of $PhCH{=}C(BO_2C_3H_6)_2$ to $PhCH_2CO_2H$ [2]. The ethylene glycol boronic ester $C(BO_2C_2H_4)_4$ is known [6] and was at first thought too insoluble in tetrahydrofuran (THF) to be suitable for generation of the lithio derivative, $Li^+\,{}^-C(BO_2C_2H_4)_3$ (V). Recently, V was generated using THF/dichloromethane mixtures to improve the solubility of the precursor, and condensation of V with 4,6-dichloropyrimidine-5-carboxaldehyde proved more efficient than the corresponding condensation of I [7].

In a brief exploration to extend the condensation of V to other aldehydes and ketones, benzaldehyde was chosen as the test reagent. Reaction of methyllithium with $C(BO_2C_2H_4)_4$ was tested in 1/1 and 3/1 THF/dichloromethane and in pure THF, with the best yield (85%) and easiest product to purify obtained in pure THF.



(V)

The reason for the difference between this and the previous result [7] is not known. Similar condensations of V were carried out with acetone, which gave the previously reported $(CH_3)_2C{=}C(BO_2C_2H_4)_2$ [1] in much improved yield (76%), and with cyclohexanone (83%). Although these yields are not quite as high as those of the corresponding propanediol esters reported previously [2] and duplicated closely in the present work, it may be concluded that in general the ethylene glycol esters $RR'C{=}C(BO_2C_2H_4)_2$ are readily accessible compounds.

Experimental

All manipulations of carbanions were carried out under argon. Tetrahydrofuran was rigorously dried over sodium and distilled. Methyllithium was analyzed by titration with 2-propanol to the phenanthroline endpoint. Other chemicals were reagent grade. ^{1}H NMR spectra were recorded on a Varian EM-360, with internal tetramethylsilane, and selected curves are illustrated in A. Mendoza's Ph.D. thesis, Washington State University, 1977. Elemental analyses were by Galbraith Laboratories, Knoxville, Tennessee, and are summarized in Table 3.

1,1-Bis(chloromercuri)-1-alkenes (III)

A suspension of 4.0 g (11.3 mmol) of tetrakis(trimethylenedioxyboryl)methane [6] in 50 ml of tetrahydrofuran was stirred at —70°C during dropwise addition of an equivalent amount of 1.6 *M* methyllithium in ether, warmed to 0°C and cooled to —70°C, treated with 11.3 mmol of the aldehyde or ketone, and stirred 16 h at 20—25°C, as described previously [2]. The solvent was removed under vacuum, the residue was treated with 50 ml of chloroform and 100 ml of ether, the by-product lithium salt was removed by filtration, and the solution was concentrated under vacuum to yield the crude alkene-1,1-diboronic ester (II). The boronic ester II was dissolved in 50 ml of methanol and stirred during the addition of a solution of 6.16 g (22.6 mmol) of mercuric chloride and 1.85 g (22.6 mmol) of sodium acetate in 25 ml of 50% aqueous methanol. The 1,1-bis(chloromercuri)-1-alkene (III) precipitated immediately and, after stirring a few minutes, was filtered and washed with several portions of methanol.

Diiodomethylenecyclohexane (IV)

To a solution of 3.0 g (11.4 mmol) of bis(trimethylenedioxyboryl)methylenecyclohexane [2] in 70 ml of tetrahydrofuran at 0°C was added 23 ml of 3 *M* aqueous sodium hydroxide followed by a solution of 2.96 g (27.4 mmol) of iodine in 80 ml of ether. The mixture was stirred at 0°C for 1.5 h. The excess iodine was removed by treatment with aqueous sodium thiosulfate and the ether solution was washed with water, dried over magnesium sulfate, and distilled. The product (IV) distilled at 87—88°C (0.2 mmHg), 2.79 g (71%), ^{1}H NMR ($CDCl_3$) δ 2.2—2.65 (m, 4, $=C\underline{H}_2$—), 1.35—1.8 ppm (m, 6, $(C\underline{H}_2)_3$).

Lithium tris(ethylenedioxyboryl)methide (V) and 1,1-bis(ethylenedioxyboryl)-1-alkenes

A suspension of 2.0 g (6.8 mmol) of tetrakis(ethylenedioxyboryl)methane [6] in 80 ml of tetrahydrofuran at —70°C was treated with 4.5 ml of 1.6 *M* methyllithium in ether, warmed to 0°C and cooled to —75°C, and the suspension of V treated with 6.5 mmol of the aldehyde or ketone and stirred at 20—25°C for 4 h. Other details of the procedure were similar to the synthesis of II [2]. However, the by-product lithium salt, $(Li^+\,{}^-OBO_2C_2H_4)_x$, in this case was insoluble in tetrahydrofuran and was filtered off. Evaporation of the solvent left residues of the 1,1-bis(ethylenedioxyboryl)-1-alkenes, which were further purified

TABLE 3

ELEMENTAL ANALYSES

Compound	Analysis (found (calcd.) (%))			
	C	H	Hg	Cl or other
$(C_2H_5)_2CHCH{=}C(HgCl)_2$	15.04	2.11	70.77	12.33
	(14.79)	(2.13)	(70.60)	(12.48)
$C_6H_5CH{=}C(HgCl)_2$	17.01	0.98	69.62	12.08
	(16.73)	(1.05)	(69.86)	(12.35)
$(CH_3)_2C{=}CHC(CH_3){=}C(HgCl)_2$	14.97	1.78	70.72	12.18
	(14.85)	(1.78)	(70.85)	(12.52)
$C_2H_5O_2CC(CH_3){=}C(HgCl)_2$	12.19	1.66	68.50	11.97
	(12.33)	(1.38)	(68.67)	(12.14)
$(CH_2)_5C{=}C(HgCl)_2$	15.04	1.70	71.02	12.35
	(14.85)	(1.78)	(70.85)	(12.52)
$H_2C{=}C(HgCl)_2$ (impure)	4.83	0.39	79.30	15.43
	(4.82)	(0.40)	(80.54)	(14.24)
$(CH_2)_5C{=}CI_2$	24.10	3.01		I 72.84
	(24.16)	(2.90)		(72.94)
$C_6H_5CH{=}C(BO_2C_2H_4)_2$	58.96	5.84		B 9.00
	(59.10)	(5.79)		(8.87)
$(CH_2)_5C{=}C(BO_2C_2H_4)_2$	55.77	7.76		B 9.35
	(56.01)	(7.69)		(9.17)

by treatment with 1/2 chloroform/ether and filtering [2] followed by recrystallization from ether/pentane. The product from acetone, $(CH_3)_2C{=}C(BO_2C_2H_4)_2$, was obtained in 76% yield; recrystallized, m.p. 101—102°C, reported [1] 101°C. That from benzaldehyde, $PhCH{=}C(BO_2C_2H_4)_2$, 85%; m.p. 79—80°C; ^{1}H NMR ($CDCl_3$) δ 4.34 (s, 8, $OC\underline{H}_2$), 7.3—7.7 (m, 5, $C_6\underline{H}_5$), 8.02 (s, 1, $=C\underline{H}-$). That from cyclohexanone, $(CH_2)_5C{=}C(BO_2C_2H_4)_2$, 83% yield; m.p. 62—63°C; ^{1}H NMR ($CDCl_3$) δ 1.4—1.9 (m, 6, $(C\underline{H}_2)_3$), 2.3—2.7 (m, 4, $=CC\underline{H}_2-$), 4.28 ppm (s, 8, $OC\underline{H}_2$), For analytical data, see Table 3.

Acknowledgment

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