Preparation of **9** partially labeled with ^{13}C at C-3 was achieved by reaction of diphenylketene with 2-diazoacetophenone-2-^{13}C, itself prepared from benzoyl chloride and $^{13}CH_2N_2$; in the nmr spectrum of labeled **9** the upfield ^{13}C satellite of the vinylic proton signal at δ 6.33 ($J_{^{13}C-H}$ = 182 Hz) showed the presence of 27 ± 1% ^{13}C-3. Reaction of labeled **9** with *tert*-butyllithium gave **10** labeled at C-2; both ^{13}C satellites of the methylene proton signal at δ 4.18 could be observed ($J_{^{13}C-H}$ = 129 Hz) and showed the presence of 28 ± 1% ^{13}C-2. Rearrangement of labeled **10** with sodium methoxide gave labeled **11**, in whose nmr spectrum the methylene proton signal at δ 3.81 was accompanied by observable upfield and downfield ^{13}C satellite signals ($J_{^{13}C-H}$ = 129 Hz), showing the presence of 28 ± 1% ^{13}C-3. Thus, C-2 of **10** becomes C-3 of **11** in accord with rearrangement *via* homoenolate ions analogous to **3** and **4**,[11] but not *via* 1,2-phenyl migration.

Acknowledgment. We thank the National Research Council of Canada for generous support for this investigation.

(11) A more concerted pathway is not excluded. In this regard, it is of interest to note the relationship of the rearrangement to the acid-catalyzed rearrangement of santonic acid to parasantonide.[12]

(12) R. B. Woodward and E. G. Kovach, *J. Amer. Chem. Soc.*, 72, 1009 (1950).

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The Facile Redistribution of Trialkylboranes with Trimethylene Borate. A Simple, General Synthesis of Alkaneboronic Esters and Acids from Olefins *via* Hydroboration

Sir:

Trialkylboranes undergo a facile and clean redistribution reaction with trimethylene borate under the influence of catalytic quantities of diborane at 120°. The alkaneboronic esters, formed in this reaction in nearly quantitative yields, are stable, readily isolated, and are easily hydrolyzed to the corresponding alkaneboronic acids. Consequently, this procedure provides a convenient new synthesis of alkaneboronic acids.

Alkaneboronic acids and their esters are generally prepared by the reaction of appropriate organometallics with borate esters.[1] Previously, we attempted to provide a new route to these derivatives by achieving a partial reaction of borane in tetrahydrofuran (THF) with olefins.[2] However, with only a few exceptions, the hydroboration reaction exhibits a marked preference to proceed to the trialkylborane.[3] Attempts to redistribute the trialkylboranes with excess borane in THF were also not completely satisfactory.[2]

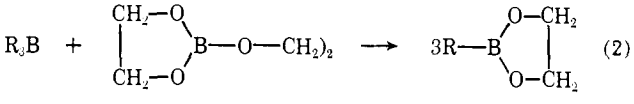
Organoboranes have been redistributed with boric oxide,[4] and with trimethoxyboroxine.[5] These reactions could provide a convenient route to the alkaneboronic acids. Unfortunately, the reactions are quite slow, requiring a temperature of 200° for a reasonable rate, so that is is not applicable to many organoboranes which can undergo isomerization at this temperature.[6]

A more promising approach appeared to be the redistribution of organoboranes with methyl borate, catalyzed by dialkylboranes[7] (eq 1).

$$n\text{-}Bu_3B + 2B(OCH_3)_3 \xrightarrow{100^\circ} 3n\text{-}BuB(OCH_3)_2 \qquad (1)$$

Indeed, this procedure appeared quite satisfactory for normal alkyl derivatives. However, the redistribution proved to be very slow with organoboranes from internal and cyclic olefins. A further difficulty appeared in storing the reaction products, $RB(OCH_3)_2$, for any length of time. They exhibited a tendency to undergo further redistribution, yielding other derivatives of boron.

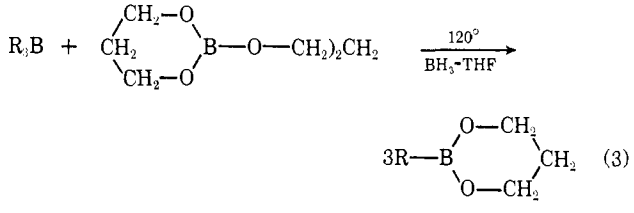
It appeared that some of these difficulties might be circumvented by preparing the ethylene glycol esters of the boronic acids through a related redistribution of the organoborane and ethylene borate[8] (eq 2). Un-



(2)

fortunately, this procedure suffered from two difficulties. First, the synthesis of ethylene borate is accompanied by the formation of considerable amount of polymer. Second, the redistribution reaction was slow and incomplete.

All of these difficulties were resolved through the use of trimethylene borate. The ester was readily synthesized in essentially quantitative yield from boric acid and trimethylene glycol. The redistribution reaction, catalyzed by 5 mol % diborane in THF, proceeded rapidly and completely at 120° (eq 3). The redistribu-



(3)

tion reaction was quite general, being equally effective for organoboranes from straight-chain olefins, such as 1-butene and 1-pentene, isoalkenes, such as isobutylene, internal olefins, such as 2-butene, cyclic olefins, such as cyclopentene and cyclohexene, and even bicyclic olefins, such as norbornene. The results are listed in Table I.[9] The products were readily recovered by distillation from the reaction mixture. Samples have been stored in ampoules for extended periods of time (up to 6 months) without detectable modification.

The esters are readily converted to the corresponding boronic acids by hydrolysis with water.

A representative redistribution reaction is that involving tri-*exo*-norbornylborane. Norbornene (14.1

(1) K. Torssell in "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McCloskey, Ed., Pergamon Press, New York, N. Y., 1964, Chapter 9.

(2) H. C. Brown, A. Tsukamoto, and D. B. Bigley, *J. Amer. Chem. Soc.*, 82, 4703 (1960).

(3) H. C. Brown and G. J. Klender, *Inorg. Chem.*, 1, 204 (1962).

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(5) P. A. McCusker and J. H. Bright, *J. Org. Chem.*, 29, 2093 (1964).

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(7) R. Koster, *Angew. Chem.*, 73, 66 (1961); B. M. Mikhailov and L. S. Vasil'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1756 (1962).

(8) R. Koster, *Angew. Chem.*, 71, 31 (1959).

(9) All the new compounds were analyzed by ir, nmr, and mass spectroscopy and gave satisfactory carbon and hydrogen analyses.

Table I. Synthesis of Alkaneboronic Esters (2-Alkyl-1,3,2-dioxaborinanes) *via* the Redistribution Reaction of Trialkylboranes with Trimethylene Borate

2-Alkyl-1,3,2-dioxaborinanes, alkyl substituent, R	—Physical properties— Bp, °C (mm)	n^{20}D	—Yield, %— Glpc	Isolated
n-Butyl	94 (50)	1.4263[a]	95	80
Isobutyl	86–87 (50)	1.4218	100	88
sec-Butyl	87 (50)	1.4263	95	85
n-Pentyl	92 (40)	1.4315	100	90
Cyclopentyl	85–86 (10)	1.4573	90	80
Cyclohexyl	93–94 (6)	1.4628	100	90
exo-Norbornyl	63–64 (0.5)	1.4783	100	86

[a] A. Finch, P. J. Gardner, J. C. Lockhart, and E. J. Pearn (*J. Chem. Soc.*, 1428 (1962)) report bp 166° (760 mm); n^{25}D 1.4205.

g, 150 mmol) was dissolved in 25 ml of THF and hydroborated with borane in THF (50 mmol of borane). The THF was removed by distillation. Trimethylene borate[10,11] (12.2 g, 50 mmol), borane (10 mmol) in THF, and a hydrocarbon internal reference were then introduced with the aid of a hypodermic syringe into the reaction vessel containing the tri-*exo*-norbornylborane. The reaction mixture was heated at 120° for 4 hr with stirring.[12] Glpc examination at this time indicated the formation of 2-*exo*-norbornyl-1,3,2-dioxaborinane in quantitative yield. The reaction mixture was cooled and the residual diborane transformed with 1,3-propanediol (608 mg, 8 mmol). The distillation provided 23.2 g (129 mmol, 86%) of the pure product.

The preparation of the alkaneboronic acids through this route is illustrated by the following synthesis of 1-butaneboronic acid. 2-*n*-Butyl-1,3,2-dioxaborinane (7.1 g, 50 mmol) was heated with 20 ml of water for 15 min. Upon cooling with ice, 4.6 g (90%) of 1-butaneboronic acid was obtained as white leaflets, mp 91–92° (sealed tube); lit.[13] mp 90–92°.

Consequently, the present reaction sequence offers a new and convenient method for the conversion of olefins into alkaneboronic esters and acids. The utilization of these important organoborane intermediates[14] in the development of novel synthetic methods is currently under investigation.

(10) A. Finch, J. C. Lockhart, and E. J. Pearn, *J. Org. Chem.*, **26**, 3250 (1961).
(11) A. J. Hubert, B. Hargitay, and J. Dale, *J. Chem. Soc.*, 931 (1961).
(12) An 8-hr heating period was necessary in the case of *sec*-butyl and cyclopentyl derivatives. No observable rearrangement[6] had occurred under these conditions in the former case, as the alkaline hydrogen peroxide oxidation of the product, upon glpc examination, gave 2-butanol with only traces of 1-butanol present.
(13) J. R. Johnson and M. G. Van Campen, Jr., *J. Amer. Chem. Soc.*, **60**, 121 (1938).
(14) D. S. Matteson, *Accounts Chem. Res.*, **3**, 186 (1970).
(15) Postdoctorate Research Associate on Grant No. GM-10937 supported by the National Institutes of Health.
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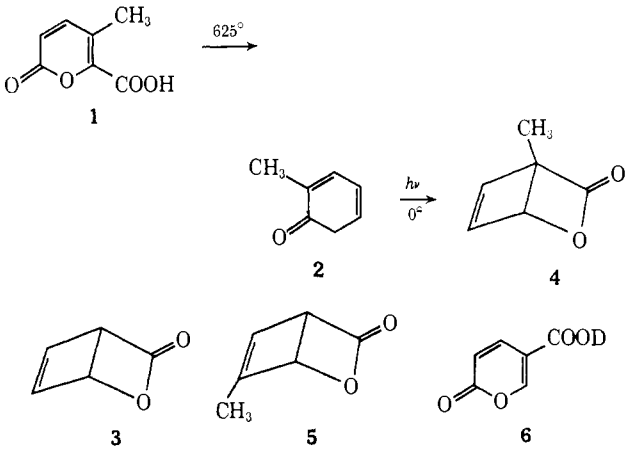
Skeletal Rearrangements of 2-Pyrones Involving 1,5-Sigmatropic Hydrogen Shifts

Sir:

During the pyrolytic decarboxylation of 5-methyl-6-carboxypyrone (**1**) we have noted apparent migration of the methyl group. Closer study of the high-temperature reactions of other substituted 2-pyrones indicates that these "migrations" are general and occur *via* a deep-seated rearrangement which is not only interesting but is relevant to several recent papers on the chemistry of 2-pyrones.

In 1941, Fried and Elderfield reported[1] that high-temperature decarboxylation of 5-methyl-6-carboxy-2-pyrone (**1**) over copper affords 5-methyl-2-pyrone. Through nmr, we have found this decarboxylation (625°, 1 Torr) actually affords 3-methyl-2-pyrone (**2**) even when silicon carbide chips or clay plate shards replace the copper powder.[2] Although this rearrangement leads one to suspect the assigned structure of **1**, the assignment is nevertheless correct. The observation of a 9.5-Hz spin–spin coupling between two vinyl protons of the acid established substituent location; prior work[4] has shown that substituted 2-pyrones show J_{34} = 9.0–10.5 Hz, J_{45} = 5.5–6.8 Hz, J_{56} = 5.0–5.2 Hz. The decarboxylation product, **2**, shows vinyl couplings of 6.3 and 5.1 Hz. Additionally, ultraviolet irradiation of dilute ethereal solutions of **2** affords a photoproduct having nmr spectral parameters which correlate well with those of bicyclo[2.2.0]pyran-2-one[5,6] (**3**) when spectral assignments are based upon structure **4** but not upon structure **5**.



A related rearrangement is observed on decarboxylation[3] of coumalic acid-*d* (**6**) for the product consists of essentially equal amounts of 2-pyrone-*3*-*d* and 2-pyrone-*5*-*d* plus some unlabeled 2-pyrone. The ratio (32:29:39) of the three products was determined by integration of the nmr spectra of the bicyclic lactones formed on irradiation of the pyrone mixture. Mass

(1) J. Freid and R. C. Elderfield, *J. Org. Chem.*, 6, 566 (1941).
(2) Neither Elderfield's original procedure nor that of Zimmerman[3] affords enough 5-methyl-2-pyrone to be detectable by nmr. The latter procedure entails the sublimation of the acid through a tube maintained at 625° and filled with copper turnings, clay plate shards, etc. Any temperature high enough to cause decarboxylation also affords "migration."
(3) H. E. Zimmerman, G. L. Grunewald, and R. N. Paufler, *Org. Syn.*, 46, 101 (1966).
(4) W. H. Pirkle and M. Dines, *J. Heterocycl. Chem.*, 6, 1 (1969).
(5) E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, **86**, 950 (1964).
(6) W. H. Pirkle and L. H. McKendry, *ibid.*, **91**, 1179 (1969).