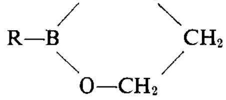
Table I. Synthesis of Alkaneboronic Esters (2-Alkyl-1,3,2-dioxaborinanes) *via* the Redistribution Reaction of Trialkylboranes with Trimethylene Borate

2-Alkyl-1,3,2-dioxaborinanes,  alkyl substituent, R	—Physical properties— Bp, °C (mm)	$n^{20}\text{D}$	—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); $n^{25}\text{D}$ 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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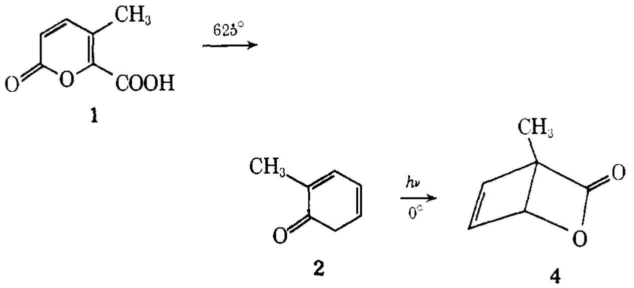
Skeletal Rearrangements of 2-Pyrones Involving 1,5-Sigmatropic Hydrogen Shifts

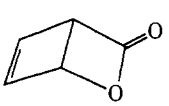
Sir:

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**.



1 **2** **4**



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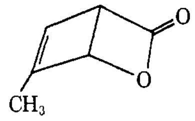

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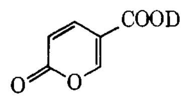


6

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).

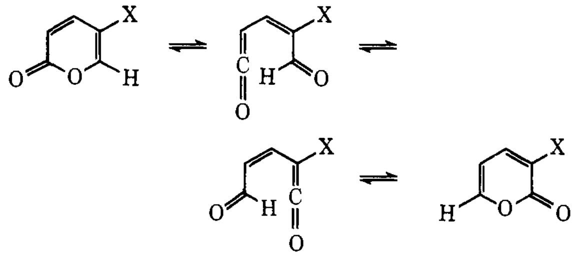
(5) E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, 86, 950 (1964).

(6) W. H. Pirkle and L. H. McKendry, *ibid.*, 91, 1179 (1969).

spectrometric analysis agrees closely with the nmr analysis concerning the amount of unlabeled 2-pyrone present and, importantly, demonstrates that less ($<4\%$) doubly deuterated 2-pyrone is present than might be expected if an intermolecular protonation–deprotonation sequence were responsible for the label scrambling.

Both of the preceding "migration" reactions have accompanied decarboxylation, an exothermic process which might conceivably supply activation energy for an otherwise rare rearrangement. To test this hypothesis, 5-bromo-2-pyrone (**7**) was sublimed (1.0 Torr) through a glass helices packed Vycor tube maintained at 530°. Nmr and glpc analysis shows the recovered material to consist of a 54:46 mixture of 3-bromo-2-pyrone (**8**) and 5-bromo-2-pyrone (**7**). Similar pyrolysis of **8** affords a 57:43 mixture of the two isomers.[7]

The previous rearrangements may be rationalized by invoking initial decarboxylation (where relevant) followed by reversible electrocyclic ring opening of the pyrones to ketene aldehydes which undergo reversible 1,5-sigmatropic shifts of the aldehydic protons (see eq 1).



When the "migrating" substituent is deuterium, the sigmatropic shift is degenerate and essentially equal amounts of the *3-d*$_1$ and *5-d*$_1$ pyrones are present at equilibrium. If the substituent is such that the shift is not degenerate, the position of equilibrium may favor one of the two possible products. This would appear to be the case in the rearrangement of 5-methyl-2-pyrone after its (presumed) formation by decarboxylation of **1**.

The ketene aldehyde postulated here as an intermediate has, in all probability, been directly observed[6] by low-temperature infrared spectroscopy. Irradiation of 2-pyrone in a 2:1 methylene chloride–tetrahydrofuran glass at −190° gives rise to absorption at 4.70 μ which disappears if the glass is allowed to warm to −80°. The ketene aldehyde responsible for the absorption may be trapped with methanol. Since this photochemically generated ketene is formed from a singlet excited state,[8] it may be that internal conversion simply affords vibrationally excited 2-pyrone which can undergo the ring-opening reaction. Hence, the photochemical and pyrolytic ring openings may be closely related. However, the 1,5-sigmatropic shift does not follow the photochemically induced ring opening,[6] presumably owing to a lack of activation energy. The requisite activation energy apparently can be acquired at ~500° and the sigmatropic shift consequently follows the pyrolytic ring-opening reaction.

DeJongh,[9] endeavoring to establish correlations between the behavior of organic molecules upon pyrolysis and upon electron impact, has recently commented on the fact that pyrolytic decarbonylation of 2-pyrone at 900° affords furan while the decarbonylation of the 2-pyrone molecular radical cation affords a C_4H_4O radical cation reported[10] not to be furan-like. Since the present work makes it clear that 2-pyrones undergo ring opening at high temperatures, it is interesting to speculate whether DeJongh's pyrolytic decarbonylation occurs directly from 2-pyrone or from the ring-opened ketene aldehyde **9**. Decarbonylation of the ketene may afford furan, perhaps *via* the intermediacy of a carbene.

One may also speculate as to whether 2-pyrones undergo the ring-opening and 1,5-hydrogen shift reactions on electron impact. Without asserting this to be so, we point out that this type of behavior would cause scrambling of deuterium between the 3 and 5 positions of 2-pyrone but maintain the uniqueness of deuterium in either the 4 or the 6 position. This is the experimentally observed result.[10]

Acknowledgment. This work was supported by an unrestricted Du Pont Young Faculty Grant.

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(7) Identifications were made by melting point and nmr spectroscopy. See W. H. Pirkle and M. Dines, *J. Org. Chem.*, **34**, 2239 (1969).

(8) W. H. Pirkle and L. H. McKendry, *Tetrahedron Lett.*, 5279 (1968).

(9) D. A. Brant, J. D. Hribar, and D. C. DeJongh, *J. Org. Chem.*, **35**, 135 (1970).

(10) W. H. Pirkle and M. Dines, *J. Amer. Chem. Soc.*, **90**, 2318 (1968).

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Perfluorophenylsilver[1]

Sir:

We wish to report the preparation of perfluorophenylsilver, the first example of a perfluorinated aromatic silver compound,[2] (1) from perfluorophenyllithium and silver trifluoroacetate, and (2) from perfluorophenyl bromide and perfluoroisopropylsilver.[5,6]

$$CF_3CF{=}CICF_3 + (CF_3)_2CFAg \xrightarrow{CH_3CN} CF_3CF{=}C(CF_3)Ag + (CF_3)_2CFI$$

Halogen-metal exchange, reaction 2,[6] does not appear to have been observed previously with an organosilver compound.

$$C_6F_5Li + CF_3COOAg \longrightarrow C_6F_5Ag + CF_3COOLi \qquad (1)$$

$$C_6F_5Br + (CF_3)_2CFAg \longrightarrow C_6F_5Ag + (CF_3)_2CFBr \qquad (2)$$

Perfluorophenylsilver is much more stable than phenylsilver, which decomposes at about −18°,[3] and

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(1) Presented in part at the 5th International Symposium on Fluorine Chemistry, Moscow, July 1969; Abstracts of Papers, p 85.

(2) Recently, Smith and Massey have reported the preparation of lithium bis(pentafluorophenyl)silver, mp 68–74°, from C_6F_5Li and AgCl at −78°, and stated that pentafluorophenylsilver was formed "as a white solid" by its exposure to "wet air or damp solvents." [3] Perfluorophenylsilver has also been postulated as an intermediate in the reaction of pentafluorophenylhydrazine and silver oxide.[4]

(3) V. B. Smith and A. G. Massey, *J. Organometal. Chem.*, **23**, C-9 (1970).

(4) J. M. Birchall, R. N. Hazeldine, and A. R. Parkinson, *J. Chem. Soc.*, 4966 (1962).

(5) W. T. Miller, Jr., and R. J. Burnard, *J. Amer. Chem. Soc.*, **90**, 7367 (1968).

(6) *trans*-Perfluoro-1-methylpropenylsilver[7a] has also been prepared by exchange with perfluoroisopropylsilver (unpublished work with R. H. Snider).

(7) (a) W. T. Miller, R. H. Snider, and R. J. Hummel, *J. Amer. Chem. Soc.*, **91**, 6532 (1969); (b) *ibid.*, ref 16.