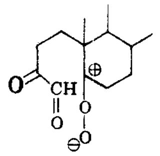
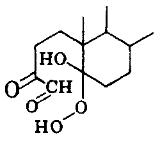
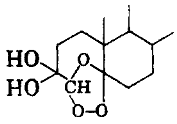
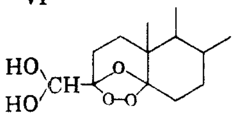
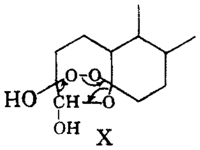

VI


VII


VIII


IX


X

VIII, IX, and X, the first two representing hydrates of normal ozonides and the last a hemiketal-acetal. On the basis of the work of Criegee,[8] IX would seem to be the preferred structure since in the presence of a protic solvent cyclic monomeric ozonides appear to form only when a bicyclo-3:2:1-system results. The formation of a stable hydrate of a carbonyl group, however, should only occur if the ozonide linkage is strongly electronegative and from the acid strength of hydrogen peroxide such seems unlikely.

At the present time, structure X would appear to represent the most probable formulation for the product.[9] The decomposition of X to products most likely follows the intramolecular pathway indicated.

## EXPERIMENTAL[10]

*Ozonization of cholestenone.* A solution of 7.78 g. (20.2 mmoles) of cholestenone, 135 ml. of C.P. ethyl acetate, 135 ml. of glacial acetic acid, and 8 ml. of water was cooled in an ice salt bath and then 2.5 mole-equivalents (at 0.5 mmole/min.) of ozone was passed through the solution. After standing at room temperature for 1 hr., the solution began to deposit white crystals and by removal of three fourths of the solvent under reduced pressure (20-mm. pressure at room temperature), a total of 5.0 g. (55%), m.p. 112–115° (dec.), of white crystalline solid was obtained. The crude material was dried for 24 hr. at room temperature under 20-mm. pressure. The dried material first melts at 117° with evolution of gas and then solidifies and remelts at 152–153°, the melting point of authentic seco-keto-acid V.[11] The infrared spectrum possessed bands at 2.94 μ (OH) and at 9.2, 9.5, 9.6 μ (ether—O).

*Anal.* Calcd. for $C_{27}H_{46}O_5$: C, 71.96; H, 10.29; peroxide, 7.10; mol. wt. 450.6. Found: C, 71.26; H, 10.50; peroxide, 6.86; mol. wt.[12] 439–481.

When the ozonide was heated with benzene and the solvent distilled and collected in an ice-cooled receiver, the residue after recrystallization from hexane amounted to 86% of the expected *seco-nor*-acid, m.p. 150–152°. To the benzene distillate (200 ml.) were added 2 ml. of glacial acetic acid and 4.8 g. of mercuric acetate and the mixture was refluxed for 3 hr. The evolved $CO_2$ was swept with nitrogen into a gas collection flask containing sodium hydroxide ($CO_2$-free). Precipitation of $CO_2$ as $BaCO_3$ with $BaCl_2$ yielded 70% of theory, based upon the oxidation of one mole of formic acid.

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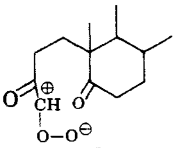
[8] R. Criegee, A. Kerchow, and H. Zinke, *Ber.*, **88**, 1878 (1955).

[9] The alternate zwitterion XI, which would appear to be a less favored intermediate, upon hydration and cyclization would give rise to a similar series of structures. Such structures cannot be differentiated from the above on the basis of the present work.


XI

[10] All melting points corrected. Analyses by the Microanalytical Laboratory, University of California.

[11] R. Tschesche, *Ann.*, **498**, 185 (1932); R. B. Turner, *J. Am. Chem. Soc.*, **72**, 579 (1950).

[12] The mol. wt. determination was kindly performed for us by Professor P. S. Bailey, University of Texas, by the cryoscopic method using dioxane as solvent.

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# Preparation of Trialkylboranes or Primary Alcohols from Pyridine-Borane and Terminal Olefins

M. Frederick Hawthorne

*Received May 12, 1958*

Two new synthetic methods for the preparation of trialkylboranes from olefins have recently been described. The first of these consists of treating the olefin with the sodium borohydride–aluminum chloride reagent of Brown and Rao.[1] The second new method is based on the direct addition of diborane to the olefin in diglyme solution at room temperature.[2] The diborane may be introduced as a gas or produced *in situ* by the reaction of sodium borohydride with boron trifluoride. The present paper describes a third method which is probably chemically similar to, but experimentally quite different from the second method above[3] and probably involves the electrophilic attack of thermally produced diborane upon the terminal olefin.

During the course of an examination of the chemistry of amine boranes it was observed that pyridine-borane would react with olefins in diglyme solvent and at temperatures near 100° to produce trialkylboranes. The reaction was conveniently carried out overnight in pressure bottles on the steam bath and with stoichiometric quantities of reactants.

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[1] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956).

[2] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

[3] It was pointed out by a referee that Dr. R. Koster reported to the Inorganic Division of the XVIth International Congress of Pure and Applied Chemistry, Paris, France, that he had successfully added triethylamine borane to terminal olefins. This is not apparent in the abstracts (page 161) of the meeting.

TABLE I

HYDROBORINATION OF OLEFINS WITH PYRIDINE-BORANE

| | | Trialkylborane | | | | | Alkanol | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Analysis | | | | | | | |
| | | % C | | % H | | | | | |
| Olefin | Yield, % | Calcd. | Found | Calcd. | Found | B.P., °C. | Identity | Yield, % | B.P., °C. |
| 1-Octene | 82 | 82.24 | 81.85 | 14.67 | 14.55 | 166 (1.5 mm.) | 1-Octanol | 90 | 190–200 |
| 1-Hexene | 70 | 81.18 | 80.90 | 14.76 | 14.66 | 127 (1.5 mm.) | 1-Hexanol | 66 | 155–160 |
| 2-Methylbutene-1 | | | | | | | 2-Methylbutanol-1 | 71 | 125–128 |
| 2-Methylpentene-1 | | | | | | | 2-Methylpentanol-1 | 50 | 145–150 |
| 2,2,4-Trimethyl-pentene-1 | 67 | 82.24 | 81.95 | 14.67 | 14.60 | 135 (1 mm.) | 2,2,4-Trimethyl-pentanol-1[a] | 58 | 168–170 |
| Styrene | | | | | | | β-Phenylethanol | 57 | 90–92 (6 mm.) |
| α-Methylstyrene | 66 | 88.03 | 87.82 | 9.03 | 8.80 | 170 (10 mm.) | 2-Phenylpropanol-1 | 64 | 125–126 (7 mm.) |
| Cyclohexene | | | | | | | Cyclohexanol | 47 | |
| Cyclopentene | 60 | 82.57 | 82.20 | 12.47 | 12.19 | 140 (6 mm.) | Cyclopentanol | 55 | |

[a] Characterized as 3,5-dinitrobenzoate, m.p. 73–74° (D. J. Hadley, R. H. Hall, and D. I. H. Jacobs, *J. Chem. Soc.*, 1416 (1954), report m.p. 73–74° for this derivative).

$$\begin{tikzcd} C_5H_5NBH_3 + 3\ CH_2{=}CHR \arrow[r, "\text{diglyme}", "100^\circ"'] & C_5H_5NB(CH_2CH_2R)_3 \arrow[d, shift left] \\ & C_5H_5N + B(CH_2CH_2R)_3 \arrow[u, shift left] \end{tikzcd}$$

Acidification of reaction mixtures under a nitrogen atmosphere afforded, after extraction and washing, ethereal solutions of the corresponding trialkylborane. The borane was then isolated directly by fractionation or converted by hydrogen peroxide oxidation to the corresponding alcohol. The experimental simplicity of the method was enhanced by the use of pyridine borane, an air stable and essentially nonvolatile material which is easily prepared[4] in quantity if necessary but which is now commercially available.[5]

Table I lists the results of several representative reactions which were carried out with 0.20 mole of olefin and 0.07 mole of pyridine-borane. Several reaction mixtures were worked up to yield the trialkylboranes. In all cases a reaction mixture was directly converted to the primary alcohol by oxidation of the crude trialkylborane with hydrogen peroxide. The purified alcohols were identified by comparison of their infrared spectra with the spectra of authentic samples and by boiling point. In each case the trialkylborane produced was that which arises by addition of the borane fragment to the terminal carbon atom.[6]

The mechanism of this process probably involves the electrophilic addition of thermally produced diborane to the terminal olefin.

## EXPERIMENTAL

Pyridine-borane was prepared by the method of Taylor, Grant, and Sands[3] and melted at 10–11° after purification by fractional freezing. Material prepared in this manner was successfully stored for a year without signs of deterioration.

The olefins employed were obtained from commercial sources and fractionated before use with a 40-plate spinning band distillation column.

*Pressure vessel.* At the outset the reaction of pyridine borane with 1-octene was successfully carried out using a simple one-necked flask with a reflux condenser and a nitrogen atmosphere. However, this procedure was quite unsatisfactory when applied to the olefins of low molecular weight and low boiling point due to volatilization of the olefin. Therefore, a sealed system was employed in the form of glass pressure bottle of 200-ml. capacity and equipped with a spring held cap. In larger scale preparations an autoclave could no doubt be used to advantage.

*General procedure.* To 25 ml. of diglyme which had been dried by distillation from lithium aluminum hydride at reduced pressure under nitrogen was added 6.5 g. (0.07 mole) of pure pyridine-borane and 0.20 mole of the desired olefin. The solution was placed in the pressure bottle and the bottle swept with dry nitrogen and quickly stoppered. The pressure bottle was then placed in a steam bath for a period of 14 hr., cooled to room temperature, and the contents transferred to a separatory funnel equipped with a nitrogen inlet tube. Ice (50 g.) and 200 ml. of water were added followed by 150 ml. of ethyl ether. The mixture was then acidified with 100 ml. of 5*N* hydrochloric acid. Small quantities of hydrogen were evolved during acidification. The ether layer was washed three times with water in a nitrogen atmosphere and dried with magnesium sulphate while in the separatory funnel. The dried ether solution of trialkylborane was then transferred under nitrogen to a spinning band distillation column, the ether distilled, and the residue distilled in vacuum to yield pure trialkylborane.

*Oxidation of trialkylboranes with hydrogen peroxide.* Alternatively, the wet ethereal solution of trialkylborane was mixed with 50 ml. of 10% aqueous sodium hydroxide solu-

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[4] M. D. Taylor, L. R. Grant, and C. A. Sands, *J. Am. Chem. Soc.*, **77**, 1506 (1955).

[5] Callery Chemical Co., Pittsburgh, Pa.

[6] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1137 (1957) show that such adducts are the more stable and are readily formed.

tion and vigorously stirred at the ether reflux temperature as 100 ml. of 20% hydrogen peroxide was added dropwise. After the oxidation step the ether layer was separated, washed with water, and then with a 5% ferrous ammonium sulfate solution until no further coloration of the aqueous layer occurred. The ether layer was then dried over magnesium sulfate and distilled through the spinning band column to yield the pure alcohol.

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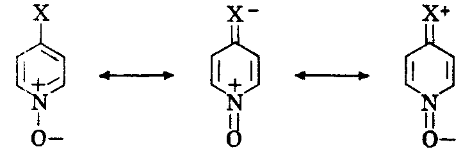
## The Basicities of Substituted Pyridine-1-oxides. A Reaction Series Requiring Use of $\sigma^+$ and $\sigma^-$ [1]

H. H. Jaffé

*Received May 12, 1958*

Some years ago we determined and examined the basicities of a series of substituted pyridine-1-oxides.[2] We recognized at that time that resonance between structures I, II, and III was important.[2a] II was expected to make a particularly important contribution when X was electron attracting by a tautomeric effect (*e.g.* —$NO_2$, —COOR), and in the treatment of the data by the Hammett equation[3] we consequently used $\sigma^-$-values[4] for these substituents. Similarly, we recognized that structure III would make a particularly large contribution to the resonance hybrid when X was capable of electron release by a tautomeric effect (*e.g.* —OR, —$NR_2$), and we assumed that the failure of the experimental points for 4-hydroxypyridine-1-oxide, 4-aminopyridine-1-oxide, and isoquinoline-1-oxide to fall on the line defined by the plot of the $pK_a$'s[5] of the other compounds *vs.* $\sigma$-values was due to this reason. At that time, however, no special substituent constants were available for tautomerically electron releasing substituents in conjugation with electron withdrawing side chains or reaction centers, and hence we were unable to adequately deal with the $pK$'s of the three compounds mentioned in terms of the Hammett equation. The recent introduction of such constants ($\sigma^+$) by Brown and Okamoto[6] and by Deno and Evans[7] and the discussion of the tautomeric equilibria in 4-hydroxy- and 4-aminopyridine-1-oxides by Gardner and Katritzky[8] have prompted us to re-examine our data.



I II III

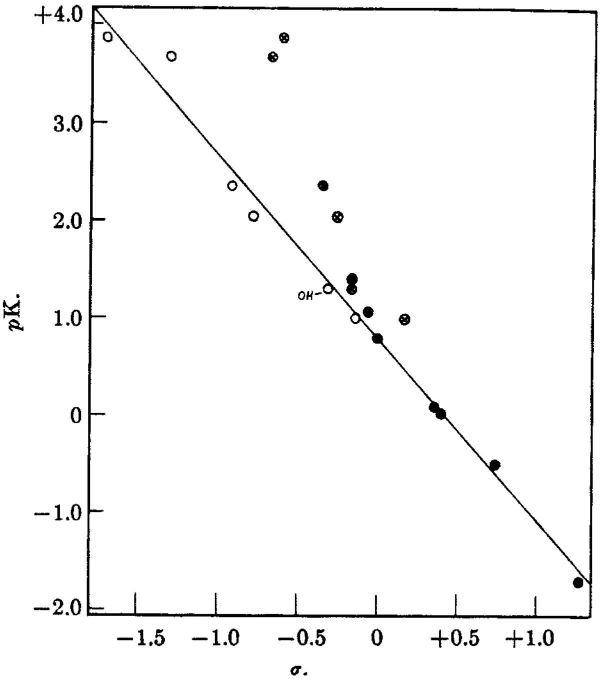


Fig. 1. Plot of the $pK_a$'s of 1-hydroxypyridinium ions against $\sigma$. Open circles, $\sigma^+$ values; crossed circles, normal $\sigma$-values; full circles, normal $\sigma$-values or $\sigma^-$-values for groups for which $\sigma^+$ is not applicable

Fig. 1 shows a plot of our $pK_a$-values against $\sigma$; $\sigma^-$-values are used for electron withdrawing, $\sigma^+$-values for electron releasing substituents. Since the data of Gardner and Katritzky were in reasonable agreement with ours where comparison was possible, their data are included for those compounds which we had not examined. Fig. 1 also shows (as crossed circles) the points for electron releasing substituents using the normal $\sigma$-values. The tremendous improvement in the fit resulting from the use of $\sigma^+$-values is immediately apparent. The 13 data, which cover a range of more than 5 log units are correlated with $\rho = 1.893 \pm 0.071$, $r = 0.992$, $s = 0.201$ $(-\log k^\circ)_{calc.} = 0.812$ in excellent agreement with $pK^\circ = 0.79$. Although the $\rho$-value is slightly lower than that previously reported, it still bears a striking resemblance to the value applicable to the $pK$'s of phenols. The data of Gardner

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[1] This work was supported by the office of Ordnance Research, U. S. Army.

[2] (a) H. H. Jaffé, *J. Am. Chem. Soc.*, **76**, 3527 (1954); (b) H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.* **77**, 4441 (1955).

[3] (a) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Company, Inc., New York, 1940, Chapter VII; (b) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[4] By agreement between Prof. H. C. Brown, R. W. Taft, Jr., N. C. Deno, and the author, the constants designated as $\sigma^*$ in ref. 3 b are now referred to as $\sigma^-$.

[5] As in earlier papers (ref. 2) all basicities are expressed as $pK_a$'s of the conjugate acids.

[6] Y. Okamoto and H. C. Brown, *J. Am. Chem. Soc.*, **79**, 1913 (1957); the $\sigma^+$ values used are the latest revised values of Prof. Brown.

[7] N. C. Deno and W. L. Evans, *J. Am. Chem. Soc.*, **79**, 5804 (1957).

[8] J. N. Gardner and A. R. Katritzky, *J. Chem. Soc.*, 4375 (1957).