Acknowledgment.—We are indebted to Mr. Clayton Mabuni for technical assistance. This investigation was supported by a PHS Grant GM-10413 from the Institute of General Medical Sciences, Public Health Service.

(13) N.D.E.A. Fellow, 1960–1963; NIH Predoctoral Fellow, 1963–1964.

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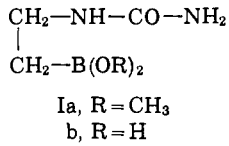
RECEIVED MAY 26, 1964

Hydroboration of Ureido-Substituted Olefins[1]

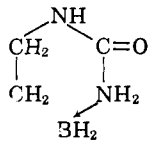
Sir:

A research program leading to the synthesis of boron compounds for neutron capture therapy[2,3] has prompted attempts directed toward the synthesis of nucleic acid bases containing boron as a ring hetero atom. This has resulted in the preparation of several ureidoalkylboronic acids inaccessible by any previously known methods. The synthesis of functionally substituted aliphatic boronic acids has been effected primarily by radical additions of vinylboronic acid derivatives.[4] The scope of the hydroboration reaction for the synthesis of such compounds is indicated in the work of Brown,[5] and some examples are realized in this report.

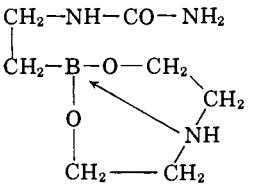
Diborane normally reacts with unhindered olefins to produce trialkylboranes.[6] However, when N-vinylurea[7] (1 mole) was treated with diborane (1.5 moles as BH_3) in tetrahydrofuran at 0° and followed by decomposition of the excess diborane and the intermediate alkylborane with excess methanol, **dimethyl β-ureidoethylboronate** (Ia), m.p. 65–68°, was formed in 80% yield. *Anal.* Calcd. for $C_5H_{13}BN_2O_3$: C, 37.54; H, 8.19; B, 6.76; N, 17.52. Found: C, 37.81; H, 8.20; B, 6.85; N, 17.72. This hygroscopic ester afforded the corresponding **boronic acid** (Ib), m.p. 102–104°, on treatment with water. *Anal.* Calcd. for $C_3H_9BN_2O_3$: C, 27.30; H, 6.88; B, 7.64; N, 21.25. Found: C, 27.35; H, 6.92; B, 7.84; N, 21.30. The n.m.r. spectrum of this acid in D_2O showed five exchangeable protons and two triplets (each of two protons, 0.96a nd 3.50, J = 15 c.p.s.), thus establishing the 1:2-disubstituted ethane structure. Both the ester Ia and the acid Ib gave the same derivative II, m.p. 237–238°, when treated with diethanolamine. *Anal.* Calcd. for $C_7H_{16}BN_3O_3$: C, 41.82; H, 8.02; B, 5.38; N, 20.89. Found: C, 42.10; H, 8.14; B, 5.71; N, 21.10.



Ia, R = CH_3
b, R = H



III



II

Using the same conditions, analogous compounds have been obtained from N-propenyl-,[8] N-cyclohexenyl-,[8] and N-allylurea, in yields ranging from 30 to 90% of theory.

The formation of these monoalkylboronic acid derivatives in such high yields rather than the usual trialkylboron compounds points to the probability of an internally stabilized intermediate such as III being involved. This type of coordination would decrease the reactivity of the monoalkylborane to further hydroboration of unsaturated centers. Thus, the reaction would terminate at this stage. The utilization of one mole of "hydride"[5b,c] per mole of olefin in the hydroboration of certain unsaturated chlorides and tosylates[5b] and the facile reduction of unsaturated esters[5c] where such cyclic entities can occur lend support to this type of coordinated monoalkylborane intermediate.

The extension of this work to other functionally substituted olefins bearing atoms which can coordinate with the introduced borane moiety in five-, six- or seven-membered intermediates is underway in these laboratories. In this manner, it is expected that the reaction will terminate at the monoalkylborane stage, thus permitting the synthesis of other substituted alkylboronic derivatives. The further interaction of the boronic acid moiety with the functional group may permit the synthesis of new boron heterocycles of potential pharmacological interest.

Acknowledgment.—The authors wish to thank William H. Sweet, M.D., Chief of the Neurosurgical Services at the Massachusetts General Hospital, for his interest and encouragement.

(8) D. N. Butler and A. H. Soloway, unpublished work. These ureas were prepared by the method used by Hart (see ref. 7) for the synthesis of N-vinylurea and satisfactory analytical data have been obtained for these compounds.

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Dihalomethylenation of Protonic Acids with Phenyl(trihalomethyl)mercury Compounds

Sir:

The dihalomethylenation by phenyl(trihalomethyl)-mercury compounds of C–H, Si–H, and Ge–H bonds,[1] as well as the halogenation of Sn–H bonds by such mercurials,[2] have been reported. We have extended our studies of the reactions of phenyl(trihalomethyl)-

(1) This investigation was supported by grants from the John A. Hartford Foundation, Inc., the U. S. Atomic Energy Commission (AT(30-1)3267), and the U. S. Public Health Service (CA 07368).

(2) A. H. Soloway, "Boron Compounds in Cancer Therapy," in "Progress in Boron Chemistry," Vol. 1, Pergamon Press, New York, N. Y., 1964, pp. 203–234.

(3) T. K. Liao, E. G. Podrebarac, and C. C. Cheng, *J. Am. Chem. Soc.*, **86**, 1869 (1964), and references cited therein.

(4) D. S. Matteson and W. H. Mah, *ibid.*, **85**, 2599 (1963).

(5) (a) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, Chapter 19; (b) H. C. Brown and K. A. Keblys, *J. Am. Chem. Soc.*, **86**, 1791 (1964); (c) H. C. Brown and K. A. Keblys, *ibid.*, **86**, 1795 (1964); (d) H. C. Brown and O. J. Cope, *ibid.*, **86**, 1801 (1964).

(6) See ref. 5a, chapter 6.

(7) R. Hart, *Bull. soc. chim. Belges*, **66**, 229 (1957).

(1) D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, **85**, 2667 (1963).

(2) D. Seyferth, H. D. Simmons, Jr., and L. J. Todd, *J. Organometal. Chem.*, in press.

mercurials with hydrogen compounds and report here some novel reactions of these mercury derivatives with protonic acids.

The cleavage of mercury–carbon bonds by acids, *e.g.*, by HCl[3] or by carboxylic acids,[4] is well documented. More pertinent is the report[5] that $C_6H_5HgCCl_3$ reacts with methanolic HCl to give chloroform and phenylmercuric chloride.

In view of this previous literature it was surprising to find that phenyl(bromodichloromethyl)mercury undergoes an apparently general reaction with carboxylic acids in benzene solution at 60–80°. Virtually quantitative yields of phenylmercuric bromide were obtained in 45 min. and isolated yields of the dichloromethyl esters were high.[6,7] The dihalomethylenation of carboxylic acids is a very rapid reaction. This was shown clearly in an experiment in which 0.036 mole each of cyclohexene and acetic acid were allowed to compete for 0.012 mole of $C_6H_5HgCCl_2Br$ in refluxing benzene (30 ml.) during 40 min.[10] G.l.c. analysis showed the products to be dichloromethyl acetate (64%) and 7,7-dichlorobicyclo[4.1.0]heptane (28%).

$$C_6H_5HgCCl_2Br + RCOOH \longrightarrow RCOOCHCl_2 + C_6H_5HgBr$$

Phenyl(bromodichloromethyl)mercury appears to dichloromethylenate alcohols as well. Heating 0.015 mole of this mercurial at 80–85° with 0.015 mole of 1-butanol in 30 ml. of ethylbenzene under nitrogen with stirring caused complete consumption of the mercurial within 30 min., and phenylmercuric bromide precipitated (85%). The volatile products (g.l.c. analysis) were *n*-butyl formate, *n*-butyl chloride, chloroform, and benzene. The first two most probably were formed by the reactions

$$C_6H_5HgCCl_2Br + C_4H_9OH \longrightarrow C_6H_5HgBr + C_4H_9OCHCl_2 \quad (1)$$

$$C_4H_9OCHCl_2 + C_4H_9OH \longrightarrow (C_4H_9O)_2CHCl + HCl \quad (2)$$

$$(C_4H_9O)_2CHCl \longrightarrow HCOOC_4H_9 + C_4H_9Cl \quad (3)$$

The sequence of reactions 2 and 3 represents known chemistry of dichloromethyl ethers.[11] The chloroform and benzene most likely were products of the reaction of HCl with the mercurial.

$$C_6H_5HgCCl_2Br + HCl \begin{cases} \longrightarrow C_6H_6 + CCl_2BrHgCl & (4) \\ \longrightarrow C_6H_5HgBr + CHCl_3 & (5) \end{cases}$$

The yields of products based on this scheme were: *n*-butyl formate, 44%; *n*-butyl chloride, 17.5%; chloroform, 29.2%; benzene, 16.7%. No improvement in the yield of the formate resulted when an excess of 1-butanol was used.

Further experiments showed that the postulated reaction 5, the "insertion" of CCl_2 into HCl, does indeed occur very readily. When dry hydrogen chloride was bubbled into a solution of $C_6H_5HgCCl_2Br$ (0.012 mole) in 30 ml. of toluene at 80°, precipitation of phenylmercuric bromide (61%) occurred, and the starting mercurial was consumed within 15 min. Analysis of the solution showed that benzene (34%) and chloroform (69%) had been formed. No bromodichloromethane could be detected. The study of the action of gaseous HCl on $C_6H_5HgCBr_3$ showed that these reactions are more complicated than the results of the $C_6H_5HgCCl_2Br$–HCl reaction indicate. Thus a similar reaction in chlorobenzene solution at 80–85° of HCl with $C_6H_5HgCBr_3$ gave benzene (83%) and the expected $CHClBr_2$ (5.3%), but also $CHCl_2Br$ (4.5%) and $CHCl_3$ (7.2%). No bromoform could be detected. Separate experiments showed that the chloroform and bromodichloromethane did not result from exchange reactions (in the presence of C_6H_5Hg halide or mercuric halides) between $CHClBr_2$ and HCl and provided evidence that such exchange took place *before* $CHClBr_2$ formation. Thus in the experiment with $C_6H_5HgCBr_3$ described above the precipitated solid and the solid obtained by evaporation of the filtrate (6.7 g. total) were mixed with 5.35 g. of diphenylmercury in 30 ml. of benzene and heated at reflux with 3.4 g. of cyclohexene. This reaction gave 7-bromo-7-chlorobicyclo[4.1.0]heptane (7.9% based on the $C_6H_5HgCBr_3$ starting material) and 7,7-dichlorobicyclo[4.1.0]heptane (4.0%), as well as the expected 7,7-dibromobicyclo[4.1.0]heptane (48.4%). These results imply that the recovered trihalomethylmercury compounds (presumably CX_3HgCl in view of the high benzene yield) contained not only CBr_3 groups, but also CBr_2Cl and $CBrCl_2$ groups; *i.e.*, exchange between HCl and $C_6H_5HgCBr_3$ and/or CBr_3HgCl had taken place. The presence of these groups on mercury make the anomalous HCl dihalomethylenation products understandable. In summary, it appears that there occur three simultaneous reactions when HCl reacts with $C_6H_5HgCBr_3$ in an aromatic solvent at *ca.* 80°: (1) phenyl–mercury cleavage; (2) CBr_2 "insertion" into the H–Cl bond; (3) Cl–Br exchange between mercurial and HCl, giving $-HgCClBr_2$, $-HgCCl_2Br$, and possibly even $-HgCCl_3$ species.[12] Subsequent reactions of these exchange products complicate things even more.

We have shown[13] that the olefin–mercurial reaction in benzene at 80° proceeds *via* free dihalocarbene. We favor also a carbene mechanism for the acid–mercurial reaction. This then would be the first example of a reaction in which dichlorocarbene reacts as a nucleophile.

$$:CCl_2 + HX \longrightarrow HCl_2C^{\oplus}X^{\ominus} \longrightarrow CHCl_2X$$

(3) M. S. Kharasch and M. W. Graffin, *J. Am. Chem. Soc.*, **47**, 1948 (1925); M. S. Kharasch and R. Marker, *ibid.*, **48**, 3130 (1926); M. S. Kharasch and A. L. Flenner, *ibid.*, **54**, 674 (1932).

(4) A. A. Bol'shakova, *Zh. Obshch. Khim.*, **24**, 266 (1954).

(5) A. N. Nesmeyanov, R. Kh. Freidlina, and F. K. Velichko, *Dokl. Akad. Nauk SSSR*, **114**, 557 (1957).

(6) For example, $CH_3COOCHCl_2$, b.p. 121–122°, δ_{CCl_2H} 7.67 p.p.m.,[8] 92%; $C_6H_5COOCHCl_2$, b.p. 75° (2 mm.), δ_{CCl_2H} 8.04 p.p.m., 86%; $ClCH_2COOCHCl_2$, b.p. 69° (6 mm.), δ_{CCl_2H} 7.72 p.p.m., 86%; $(CH_3)_3CCOOCHCl_2$, b.p. 68° (14 mm.), δ_{CCl_2H} 7.68 p.p.m., 81%.

(7) In view of the instability of dichloromethanol and the fact that chlorination of methyl esters of acids above acetic acid does not result in chlorination of the methyl group,[9] this procedure may have unique preparative applicability.

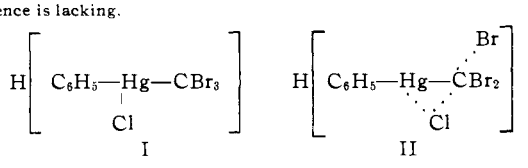
(8) N.m.r. spectra were obtained in CCl_4 solution using a Varian A60 spectrometer. Chemical shifts are given in p.p.m. downfield from tetramethylsilane.

(9) A. Bruylants, M. Tits, and R. Dauby, *Bull. soc. chim. Belges*, **58**, 310 (1949).

(10) Phenylmercuric bromide was obtained in 96% yield.

(11) A. Rieche and H. Gross, *Chem. Ber.*, **92**, 83 (1959).

(12) How such exchange occurs is not known as yet. It is tempting to write intermediates such as I or transition states such as II, but experimental evidence is lacking.



I II

(13) D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, **86**, 2730 (1964).

A comprehensive study of the reaction of phenyl(trihalomethyl)mercurials with various functional alcohols and organic acids, with oxyacids of other elements, and with other element–hydrogen compounds is in progress. The mechanisms of these reactions are under investigation.

Acknowledgment.—The authors are grateful for support of this work by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. AF-AFOSR-502-64.

(14) (a) Alfred P. Sloan Foundation Fellow, 1962–1966; (b) Postdoctoral Research Associate, 1963–1964.

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RECEIVED MAY 16, 1964

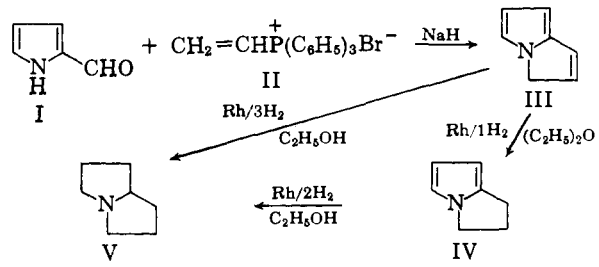
Reactions of Phosphorus Compounds. IV. Preparation of 3H-Pyrrolizine, 1,2-Dihydro-3-H-pyrrolizine, and Pyrrolizidine

Sir:

We wish to report the first synthesis of the parent 3H-pyrrolizine (III) and its reduction to 1,2-dihydro-3H-pyrrolizine (IV) and the fully saturated pyrrolizidine (V). This technique provides a superior method for the preparation in high yield of these bridgehead nitrogen heterocycles from readily available starting materials. The interest in this fused-ring system stems from the appearance of saturated and partially saturated pyrrolizine rings in many alkaloids.[1]

This synthesis was accomplished by employing the new general method developed in our laboratory for the preparation of heterocyclic and carbocyclic ring systems[2] from vinyltriphenylphosphonium bromide (II).[3]

When 2-pyrrolaldehyde[4] (I, 0.210 mole) was allowed to react with sodium hydride (0.183 mole) in anhydrous ether (200 ml., 4 hr.) followed by the addition of the salt II (0.215 mole) an exothermic reaction was observed. The resulting mixture was stirred under reflux for 24 hr. followed by filtration, concentration, and distillation. Pyrrolizine (III, 16.6 g., 87% yield) was obtained, b.p. 68–70° (15 mm.), n^{27}D 1.5745.



Redistillation on an 18-in. spinning band column gave an analytically pure sample, b.p. 65° (7.5 mm.), n^{27}D 1.5751. *Anal.* Calcd. for C_7H_7N: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.85; H, 6.60; N, 13.29. The infrared and n.m.r. spectra were consistent with the structure assigned.

Hydrogenation of pyrrolizine (III, 0.035 mole) with 5% rhodium on carbon in diethyl ether showed a rapid uptake of a quantitative amount of 1 mole of hydrogen per mole of III, and, on distillation, gave 3.04 g. (81%)[5] of 1,2-dihydro-3H-pyrrolizine (IV), b.p. 70° (20 mm.), n^{25}D 1.5267 (lit.[6] b.p. 63° (10 mm.), n^{25}D 1.5264). The infrared and n.m.r. spectra were consistent with the structure assigned.

Reduction of 1.41 mmoles of III over 5% rhodium on carbon in ethanol showed a ready absorption of 99% of 3 moles of hydrogen per mole of III. The pyrrolizine picrate (VI) was obtained directly from the filtered hydrogenation mixture, m.p. 258–260° dec. (lit.[7] m.p. 256–258° dec.). Similarly 0.05 mole of III gave 4.54 g. of pyrrolizidine, b.p. 77–84° (87 mm.), n^{27}D 1.4596, shown to be 83% V by gas phase chromatography, for an over-all yield of 68%. A pure sample (better than 99% by g.p.c.) had b.p. 79° (70 mm.), n^{30}D 1.4628 (lit.[7] b.p. 140–143° (748 mm.), n^{20}D 1.4561). A similar reduction of 1.29 mmoles of IV showed a quantitative uptake of 2 moles of hydrogen and yielded 91% VI, m.p. 260–262° dec.

Further studies on the preparation of substituted pyrrolizine systems and on the preparation of the parent pyrrolizinium salts are underway and will be reported in a future publication.

(1) W. L. Mosby, "Heterocyclic Compounds," Vol. 15, Interscience Publishers, Inc., New York, N. Y. 1961, Chapter III, and references cited therein.

(2) Previous paper in this series: E. E. Schweizer, *J. Am. Chem. Soc.*, **86**, 2744 (1964).

(3) E. E. Schweizer and R. D. Bach, *J. Org. Chem.*, **29**, 1746 (1964).

(4) Eastman Kodak Chemicals, Rochester 3, N. Y.

(5) Shown to be better than 99% pure by gas phase chromatography on a Carbowax 20 M on Haloport column from Wilkins Instrument Co.

(6) J. M. Patterson, J. Brasch, and P. Drenchko, *J. Org. Chem.*, **27**, 1652 (1962).

(7) N. J. Leonard and W. E. Goode, *J. Am. Chem. Soc.*, **72**, 5404 (1950).

(8) Public Health Service Predoctoral Fellow.

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RECEIVED MAY 27, 1964

BOOK REVIEWS

Advances in Photochemistry, Volume 1. By W. ALBERT NOYES, JR., Department of Chemistry, University of Rochester, Rochester, N. Y., GEORGE S. HAMMOND, Department of Chemistry, California Institute of Technology, Pasadena, Calif., and J. N. PITTS, JR., Department of Chemistry, University of California, Riverside, Calif. John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1963. ix + 443 pp. 15.5 × 23.5 cm. Price, $16.50.

The first volume of "Advances in Photochemistry" contains nine chapters contributed by thirteen authors of different disciplinary backgrounds. All authors are well known for their contributions in the respective fields. Recent developments of new experimental techniques, such as spectroscopy and magnetic resonance spectrometry for the identification of intermediates and products, flash photolytic spectrometry for the detection of short-lived intermediates, and chromatography for the isolation of products, promoted a mutual interest among various groups of investigators. In view of the recent interest in photochemistry, the book is a timely addition to the field.

The first chapter on "The 'Vocabulary' of Photochemistry" by J. N. Pitts, F. Wilkinson, and G. S. Hammond provides