

A NOVEL DISPROPORTIONATION OF ARYLBORONIC ACIDS¹

Michael J.S. Dewar and Ralph C. Dougherty²

Department of Chemistry, The University of Texas

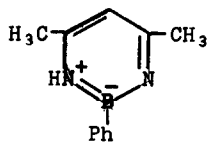
Austin, Texas 78712

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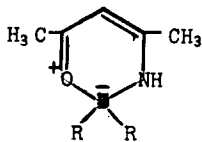
In an attempt to prepare 4,6-dimethyl-2-phenyl-2,3-borazaropyridine (I) by a reaction between acetylacetone, triphenylboroxine, and ammonia, we obtained 2,2-diphenyl-4,6-dimethyl-1H-boroxazine (IIa), a compound which could have arisen only by disproportionation of phenylboronic acid to diphenylborinic acid. This was confirmed by a synthesis of II from diphenylborinic acid, acetylacetone, and ammonia, in 82% yield, and by an experiment in which triphenylboroxine was heated alone with potassium *t*-butoxide in xylene, diphenylborinic acid being isolated as its ethanolamine derivative.

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² National Science Foundation Predoctoral Fellow; present address: Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois.



I


 II a, R = phenyl
 b, R = o-tolyl

The structure of IIa was indicated by elemental analysis (found: C, 78.00; H, 7.00; B, 3.85; N, 5.12; M.W. (thermoelectric/benzene), 270; $C_{17}H_{18}BNO$ requires: C, 77.97; H, 6.89; B, 4.11; N, 5.32%. M.W., 263), and by its proton n.m.r. spectrum. This showed multiplets at 2.86 τ (phenyl hydrogens) and 4.93 τ (ring CH), and a doublet at 8.08 τ (splitting, 7.7 c.p.s.) (methyl groups), the relative areas being the expected ratio 10:1:6. The structure IIa was also consistent with the observed infrared spectrum ($\bar{\nu}_{max}$ in carbon tetrachloride or carbon bisulphide 3390, 3345, 3070, 3055, 3010, 1625, 1545, 1434, 1392, 1364, 1194, 1179, 1150, 1049, 884, 762, 744, 732, 705, 655 cm^{-1}) and with the observed ultraviolet spectrum (λ_{max} in ethanol, 327 $m\mu$; $\log \epsilon_{327}$ 3.69).

In a typical experiment triphenylboroxine (20.0 g.) and acetylacetone (20.0 g.) were added to a mixture of potassium t-butoxide (2.5 g.) and dry toluene in a Dean and Stark apparatus and the mixture boiled in a current of dry

ammonia till no more water was evolved (24 hours), The resulting solution was washed with water and evaporated, and the residue then crystallized from aqueous ethanol to give IIa (12.4 g., 49%), which after sublimation (100°/0.003 mm.) and recrystallization from chloroform/petroleum ether had m.p. 101-101.5°.

A similar experiment, in which acetylacetone and ammonia were omitted, gave diphenylborinic acid, isolated as its ethanalamine complex. The yield in this single experiment was 45%, but this could certainly be greatly improved. No disproportionation took place in absence of potassium t-butoxide; an experiment in which triphenylboroxine was heated with acetylacetone in xylene in a current of ammonia gave phenylboronic acid (recovery, at least 95%).

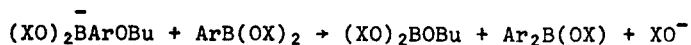
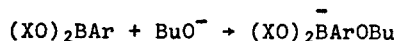
Under similar conditions tri-o-tolylboroxine reacted with potassium t-butoxide in xylene to give di-o-tolylborinic acid, characterized by its reaction with acetylacetone and ammonia to form 2,2-bis(o-tolyl)-4,6-dimethyl-1H-boraxazine (IIb), m.p. 125-125.5°, in 71% overall yield (found: C, 78.40; H, 7.19; N, 4.24. C₁₉H₂₂BNO requires C, 78.39; H, 7.56; N, 4.81%). The proton n.m.r. spectrum was consistent with this structure (multiplets at 2.48 (aryl hydrogen), 4.46 (ring hydrogen), 7.61τ (aryl methyl); doublet at 7.80τ (ring methyl) (splitting 8 c.p.s.); relative areas, 8:1:6:6).

It therefore seems likely that this disproportionation may be a general reaction for arylboronic acids. Alkylboronic

acids apparently do not react; thus butylboronic acid was recovered in over 95% yield from a similar reaction between tributylboroxine, acetylacetone, ammonia, and potassium t-butoxide.

Redistribution reactions are of course common in boron chemistry, but this seems to be the first case involving the conversion of a boronic to a borinic acid. The converse process has been observed by Abel, Gerrard, and Lappert³ who found that diphenylborinic acid disproportionates into benzene and triphenylboroxine when heated to 175° in a vacuum.

The base-catalyzed reaction reported here presumably involves transfer of aryl from a conjugate base of a derivative of an arylboronic acid;



The second step is analogous to the reaction of derivatives of arylboronic acid with organometallic reagents such as phenyllithium.

³E.W. Abel, W. Gerrard, and M.F. Lappert, J. Chem. Soc. 1451 (1958).

Apart from its intrinsic interest, this reaction may provide a convenient route to diarylboronic acids; for arylboronic acids are readily prepared by the action of organometallic reagents on alkyl borates. Existing methods for preparing diarylboronic acids are much less convenient.