at the end of 24 hours consumed sodium hydroxide equivalent in moles to 80% of the liberated chloride ion. Furthermore, 80% of the original 8-quinolineboronic acid was recovered from the neutralized solution. A mechanism involving esterification of the alcohol followed by intramolecular displacement of chloride by nitrogen therefore seems unlikely, at least insofar as the major reaction is concerned.

Experimental Part[6]

8-Quinolineboronic Acid.—A solution of 8-bromoquinoline (18 g., 0.087 mole) in 60 cc. of ether was cooled to −39° and added over a period of 20 minutes to an ether solution of butyllithium (0.216 mole) which had been cooled to −78° After a subsequent 30-minute period of stirring at this temperature, tributyl borate (76 g., 0.33 mole) in 100 cc. of ether at −39° was dropped in (20-minute period). The reaction mixture was stirred for another two hours, then allowed to warm to room temperature overnight. Cold, dilute hydrochloric acid was then added, the ether layer separated, and the aqueous layer neutralized with sodium bicarbonate. 8-Quinolineboronic acid precipitated. It was filtered off, washed, dried, and recrystallized from alcohol; m.p. higher than 300°, yield 11.85 g. (79%). The principal bands in the infrared spectrum occurred at 3.0, 6.3, 6.7, 7.3, 8.0, 8.6, 8.9, 10.5, 11.9 and 12.7 μ.

Oxidation of I.—8-Quinolineboronic acid (0.65 g.) was dissolved in 15 cc. of acetic acid and 7 cc. of water and treated with 15 cc. of 30% hydrogen peroxide at room temperature. On dilution with water and neutralization with sodium bicarbonate, 8-hydroxyquinoline (0.415 g., 76%, m.p. 69–70°) separated out as needles.

Hydrolysis of I.[7]—The boronic acid (0.630 g.) was heated with 0.5 g. of water for 36 hours at 225° in a sealed tube. Extraction of the products with ether yielded quinoline, identified as its methiodide (97% yield based on I, characterized by infrared spectrum and melting point; m.p. and mixed melting point with an authentic sample, 133–134°).

The aqueous filtrate on evaporation to dryness afforded boric acid (0.164 g., 73%).

Phenylenediamine Derivative of I.—The boronic acid (0.358 g.) and an equimolar amount of *o*-phenylenediamine (0.23 g.) were heated in refluxing benzene (50 cc.). The benzene was then removed by distillation and the residual solid recrystallized from carbon tetrachloride to give 0.50 g. (96%) of II, m.p. 188–189°. The infrared spectrum had peaks at 2.85 and 6.95 μ characteristic of the dihydrobenzoboradiazole system.[1]

Anal. Calcd. for $C_{15}H_{12}BN_3$: N, 17.15. Found: N, 17.08.

8-Quinolineboronic Acid Hydriodide.—The hydroiodide, prepared from the boronic acid and hydriodic acid in 92% yield, melted at 166–168° and titrated as a dibasic acid. (The amine salt was titrated with sodium hydroxide; subsequently mannitol was added and the addition of sodium hydroxide continued in order to titrate the boronic acids.)

Reaction of 8-Quinolineboronic Acid with Methyl Iodide.—A solution containing 13.0 g. of methyl iodide, 2.70 g. of 8-quinolineboronic acid and 200 cc. of absolute ethanol was refluxed for 15 hours. Concentration of the solution yielded 4.30 g. of a yellow solid product identical with the hydriodide prepared directly from hydrogen iodide; yield 92%, m.p. 166–168°. The analytical sample, prepared by recrystallization from ethanol, melted at 168–169°.

Anal. Calcd. for $C_9H_9O_2BNI$: B, 3.60; N, 4.66. Found: B, 3.64; N, 4.82.

By way of comparison, a solution containing 3.25 g. of quinoline, 14.85 g. of methyl iodide and 50 cc. of ethanol was refluxed for 18 hours. Removal of the solvent left 6.78 g. (99.6%) of crude product, which on recrystallization melted at 133° and had an infrared spectrum identical with that of methylquinolinium iodide.

Butyl 8-quinolineboronate was prepared by azeotropic distillation of a solution of 10 g. of *n*-butyl alcohol, 2.9 g. of 8-quinolineboronic acid and 60 cc. of benzene. Vacuum distillation of the residue yielded 2.8 g. (59%) of butyl 8-quinolineboronate, b.p. 180° (4 mm.), n^{25}_{D} 1.4840.

Anal. Calcd. for $C_{17}H_{24}O_2BN$: B, 3.79; N, 4.91. Found B, 3.6; N, 5.24.

Methiodide of Butyl 8-Quinolineboronate.—A solution of 5 g. of methyl iodide and 4.93 g. of butyl 8-quinolineboronate was warmed on a steam-bath for 12 hours; volatile material was then removed at reduced pressure, and the residue washed with ether and pentane. The hygroscopic solid which remained (7.10 g., 96%, m.p. 70–75°) titrated with alkali in the presence of mannitol as expected for butyl 8-quinoline-boronate methiodide; neut. equiv. found 420, calcd. 434. A sample of this product (2.21 g.) was subjected to steam distillation to remove butanol. Evaporation of the water left quinoline methiodide, 1.81 g. (91%), m.p. 135–136° (the melting point was not depressed when the sample was mixed with an authentic sample).

Chlorohydrins.—2-Chloroethanol (Eastman Organic Chemicals) and 3-chloro-1-propanol (Matheson) were distilled to give samples boiling at 127° (n^{20}_{D} 1.4415) and 62° (13 mm.) (n^{20}_{D} 1.4470), respectively. 4-Chloro-1-butanol, b.p. 85° (16 mm.), n^{20}_{D} 1.4520, was obtained by distillation of Eastman practical grade material.

Chloroethyl 8-Quinolineboronate.—A solution of 40 cc. of toluene, 5 g. of 2-chloroethanol and 0.82 g. of 8-quinolineboronic acid was partially distilled. On cooling, 1.31 g. (93%) of a solid ester separated, m.p. 193–194° after recrystallization from toluene.

Anal. Calcd. for $C_{13}H_{14}O_2NCl_2B$: B, 3.63; N, 4.70. Found: B, 3.69; N, 4.73.

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[6] All nitrogen analyses by Miss H. Beck.

[7] Method of E. W. Abel, W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 1451 (1958).

COMMUNICATIONS TO THE EDITOR

PRESSURE-AREA ISOTHERM FOR STEARIC ACID SPREAD WITHOUT SOLVENT

Sir:

In film-balance studies of monolayers of fatty acids and related materials, volatile solvents generally are used to aid in the spreading process. Solvents also permit accurate measurement of small quantities of monolayer-forming substances. Possible influences of such solvents on monolayers, however, are still not clear.[1,2,3] To clarify this point, pressure–area isotherms have now been obtained for stearic acid spread without solvent.

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(1) R. J. Archer and V. K. LaMer, *J. Phys. Chem.*, **59**, 200 (1955); H. S. Rosano and V. K. LaMer, *ibid.*, **60**, 348 (1956); V. K. LaMer and M. L. Robbins, *ibid.*, **62**, 1291 (1958).

(2) G. P. Semeluk, J. W. V. Hahn and J. L. Morrison, *Can. J. Chem.*, **34**, 609 (1956).

(3) H. D. Cook and H. E. Ries, Jr., *J. Phys. Chem.*, **60**, 1533 (1956).

A sensitive helical quartz spring was used to weigh a crystal of pure stearic acid of about 40 micrograms with an accuracy of 0.05 microgram. The water in a Teflon-coated film balance was heated to 71°—slightly above the melting point of stearic acid.[4] The crystal was placed on the surface between two barriers; it disappeared in a few seconds. The system was allowed to cool to room temperature, and the pressure–area isotherm was determined. In replicate experiments, reproducibility was excellent.

A typical isotherm is shown in the figure. In position and shape, it is almost identical to those obtained with *n*-hexane solvent; it differs slightly from those obtained with benzene, and only at pressures below 15 dynes. Extrapolation of the upper portion to zero pressure gives an area per molecule of 20.2 Å.^{2}, which agrees well with the values 20.0 to 20.5 obtained with benzene, *n*-hexane, and chloroform solvents.[3,5] Collapse occurs at slightly higher pressures and is less abrupt.

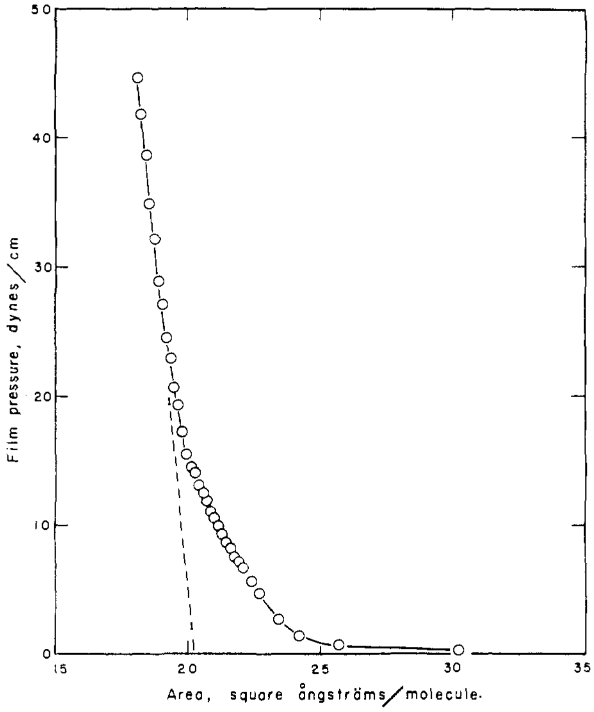

Fig. 1.—Pressure-area isotherm for stearic acid spread without solvent.

Examination of detailed plots of several such isotherms reveals that they consist of many straight-line segments, each extending through several data points. At lower pressures, the segments are short and numerous; they differ from experiment to experiment but give smiliar smoothed curves. At higher pressures, they are longer and often occur in isotherms obtained with solvents. Rapid expansion–compression reversibility has been observed along the segments and the downward extensions of them. Elastic deformation of islands or island clusters may produce such segments; changes in slope may correspond to sudden rearrangements in the monolayer when a limit of elasticity is exceeded. Such observations are not consistent with classical phase changes.[6,7]

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[4] Small crystals spread slowly at room temperature but the time required for complete spreading was prohibitive. See N. K. Adam, "The Physics and Chemistry of Surfaces," 3rd edition, Oxford University Press, London, 1941, p. 102.

[5] H. E. Reis, Jr., and H. D. Cook, *J. Colloid Sci.*, **9**, 535 (1954).

[6] N. K. Adam, "The Physics and Chemistry of Surfaces," 3rd edition, Oxford University Press, London, 1941, p. 39.

[7] W. D. Harkins, "The Physical Chemistry of Surface Films," Reinhold Publ. Corp., New York, N. Y., 1952, p. 106.

RESEARCH AND DEVELOPMENT DEPARTMENT
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RECEIVED OCTOBER 29, 1958

LITHIUM DIETHOXYALUMINOHYDRIDE AS A SELECTIVE REDUCING AGENT—THE REDUCTION OF DIMETHYLAMIDES TO ALDEHYDES

Sir:

The introduction of alkoxy substituents into lithium aluminum hydride provides a means of moderating the reducing capacity of this powerful reagent. In this way, lithium tri-*t*-butoxyaluminohydride proved to be a mild reducing agent[1] which made possible the convenient reduction of acid chlorides to aldehydes.[2] The yields of 40 to 60% realized in the case of certain aliphatic and alicyclic acid chlorides led us to examine alternative routes which would permit the synthesis of such aldehydes in higher yields by the selective reduction of carboxylic acid derivatives.

The reduction of the N-acylcarbazoles by lithium aluminum hydride has been utilized as a convenient route to the unsaturated aldehydes, $C_5H_6(CH{=}CH)_nCHO$ ($n = 2$, 4 and 6),[3] and Weygand has demonstrated that the related reduction of the N-methylanilides is applicable to a wide range of aldehyde preparations.[4] Consequently, we undertook an examination of the reduction of tertiary amides by various alkoxyaluminohydrides.

We have observed that the addition of lithium diethoxyaluminohydride (10% excess, in ether solution) to two molar equivalents of the acyldimethylamides in ether solution at 0° results in the synthesis of aldehydes in yields of 75–90% after hydrolysis. The procedure appears to be equally satisfactory, both for aliphatic and alicyclic derivatives and for aromatic. The scope of the reaction is indicated by the data in Table I.

The reagent may be synthesized conveniently *in situ* by addition of either two moles of ethanol or one mole of ethyl acetate to one mole of lithium aluminum hydride in ether solution. The synthesis of cyclohexanecarboxaldehyde given below is typical.

A solution of 20.6 g. (0.234 mole) of ethyl acetate in 250 ml. of anhydrous ether was added over a period of 2 hours to 200 ml. of a 1.17 *M* solution of lithium aluminum hydride (0.234 mole) in ether, cooled in an ice-bath. The reagent solution thus prepared was added over a period of 30 min. to a well-stirred solution of 60.6 g. (0.390 mole) of N,N-dimethylcyclohexanecarboxamide in 250 ml.

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[1] H. C. Brown and R. F. McFarlin, THIS JOURNAL, **78**, 252 (1956); **80**, 5372 (1958).

[2] H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958).

[3] G. Wittig and P. Hornberger, *Ann.*, **577**, 11 (1952).

[4] F. Weygand, *et al.*, *Angew. Chem.*, **65**, 525 (1953).