571. *The Preparation of Some Unsaturated Aliphatic Derivatives of Mercury and Boron.*

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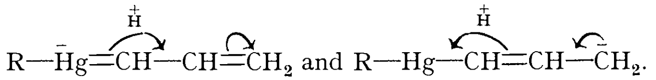
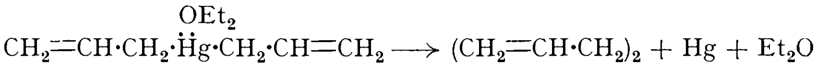
Preparation of certain unsaturated aliphatic derivatives of mercury and boron is described. Most of these substances can be obtained in small yield only and are very unstable: they tend to decompose either spontaneously or in moist air. Mercury derivatives often afford the metal whereas the oxide is the main product in the case of boron compounds.

When in their combined states mercury and boron have four and six electrons respectively in their valency shells; they present examples of non-polar atoms which could perhaps co-ordinate electrons from an attached unsaturated system in order to occupy the remaining orbitals, affording structures such as



$$R{-}\overset{-}{Hg}{=}\overset{\overset{+}{H}}{CH}{-}CH{=}CH_2 \text{ and } R{-}Hg{-}\overset{\overset{+}{H}}{CH}{=}CH{-}CH_2.$$

The stable complexes which borines and boron halides form with electron-donating groups conform with this view, as does the instability of diallylmercury, particularly when freed from ether (Vijayaraghavan, *J. Indian Chem. Soc.*, 1940, **17**, 589; 1943, **20**, 318), which quite possibly may arise from the same cause:



$$CH_2{=}CH\cdot CH_2\cdot\overset{\overset{OEt_2}{\cdot\cdot}}{Hg}\cdot CH_2\cdot CH{=}CH_2 \longrightarrow (CH_2{=}CH\cdot CH_2)_2 + Hg + Et_2O$$

In this case, however, the high resonance energy of the allyl *radical* might well lead to a considerable diminution of the dissociation energy of the carbon–mercury linkage.

Results of exploratory work on the synthesis of aliphatic allyl derivatives of the two elements discussed in this paper were disappointing: the mercury derivatives were found to be extremely unstable, and it was not possible to prepare the required dialkylallyl borines, $CH_2{:}CH\cdot CH_2\cdot BR_2$. The difficulty lies in the instability of even the saturated mixed alkyl derivatives of the two elements; indeed, only those of mercury have been isolated.

Mercury Derivatives.—Except for diallylmercury (Kharasch and Swartz, *J. Org. Chem.*, 1939, **3**, 405; Vijayaraghavan, *loc. cit.*) and analogues from a few halogen derivatives of ethylene and acetylene, unsaturated aliphatic derivatives of mercury HgRR′ are unknown. Kharasch and Swartz however have prepared allylphenyl- and allylbenzyl-mercury by interaction of allylmagnesium bromide and the appropriate mercuric chloride, R·HgCl. Allylethylmercury, now prepared in a similar way, decomposes when distilled or, rather more slowly, at room temperature.

The reverse reaction of ethylmagnesium iodide with allylmercuric iodide failed to yield allylethylmercury, the products being metallic mercury, diethylmercury, and ethylmercuric iodide. Diallyl in this case could not be isolated, but Oppenheim (*Ber.*, 1871, **4**, 671) using diethylzinc in a similar reaction was able to do so. The presence of mercury amongst the decomposition products suggests the intermediate formation of diallylmercury. This follows because ethylphenylmercury, for instance, which is known to decompose slowly yielding a mixture of diethyl- and diphenyl-mercury only (Hilpert and Grüttner, *Ber.*, 1951, **84**, 906) does not eliminate mercury. The latter, if a product of the reaction, is usually the result of the further decomposition of the diallylmercury.

The isomerisation of the allyl derivatives to prop-1-enyl derivatives failed; mild conditions left the starting material unchanged; more drastic reagents (*e.g.*, potassium *tert.*-butoxide) yielded mixtures including diallylmercury, the presence of which was inferred by its conversion into allylmercuric bromide by ethereal bromine (Vijayaraghavan, *loc. cit.*). Finally, the prop-1-enyl derivative could not be obtained by partial reduction of prop-1-ynylmercuric chloride or of diprop-1-ynylmercury. Either the molecule underwent disruption or poisoning of the catalyst occurred.

Boron Derivatives.—As noted above, mixed aliphatic borines BR_2R' have not been prepared. 2-Chlorovinylboron dichloride $Cl\cdot CH\colon CH\cdot BCl_2$ results from condensation of acetylene and boron trichloride and can be hydrolysed to the corresponding acid (Arnold, U.S.P. 2,402,509, 2,402,589/1946), whilst tri-*n*-butylborine affords, among other products, *n*-butyl dibutenylborate when halogenated with *tert.*-butyl hypochlorite (Johnson, Snyder, and Van Campen, *J. Amer. Chem. Soc.*, 1938, **60**, 115). The only other unsaturated organoboron compound, though not recognised as such, which has been isolated is the product of the reaction between diethyl zinc and triallyl borate (Councler, *J. pr. Chem.*, 1878, **18**, 371). The materials employed were evidently impure and in only one experiment was a zinc-free liquid, b. p. 110—112°, isolated. In the absence of a boron analysis, the analytical figures (C and H), which were not consistent with those required for triallylborine, appeared to fit the glyceride C_3H_5B. Repetition of the experiment afforded a product, b. p. 115—120°, the boron analysis of which corresponds to that of ethyl diallylborate (requires B, 7·9%) and not to the oxygen-free glyceride (requires B, 21·2%). Councler's experiments were carried out in the absence of a solvent; when the reaction occurred in tetralin the products were an unidentified unsaturated ester, b. p. 85—95°, and the allyl diethylborate. The methallyl ester was similarly obtained from trimethallyl borate.

There is a general tendency for reactions which are designed to yield mixed borines, *e.g.*, BR_2R', to give a mixture of the symmetrical compounds BR_3 and BR'_3 (cf. Krause, *Ber.*, 1931, **64**, 2112) and this suggested that either allyldibutylborine or a mixture of triallyl- and tributyl-borine should result from the reaction between di-*n*-butylboron bromide and allylmagnesium bromide. However, in this case the products isolated were tri-*n*-butylborine and bisdiallylboron oxide $[(C_3H_5)_2B]_2O$. The latter like other derivatives of diallylboric acid is thermally stable if distilled in oxygen-free nitrogen but slowly decomposes to boric acid in air. Bisdiallylboron oxide was also prepared from boron trifluoride and allylmagnesium bromide, and the methyl ester resulted from the reaction between the Grignard compound and methyl borate. The preparation of prop-1-enylboric acid by elimination of methanol from di-*n*-butyl 3-methoxypropylborate was unsuccessful. The yields of the unsaturated boron compounds were very low and varying amounts of boric acid were always obtained. All aliphatic boron derivatives are very sensitive to aerial oxidation and this may explain why only small amounts could be isolated.

EXPERIMENTAL

Mercury compounds.

Attempted Preparation of Prop-1-enylmercury Derivatives.—Allylmercuric iodide was deposited unchanged when its solution in hot aqueous sodium hydroxide cooled. The substance is stable to cold concentrated hydrochloric acid but the liquid evolves an unsaturated gas, probably propylene, when heated. There was no condensation when the mercury compound was mixed with freshly distilled benzaldehyde and a drop of piperidine. Warming it with potassium *tert.*-butoxide in *tert.*-butyl alcohol yielded a dark grey solution with the characteristic odour of diallylmercury. The addition of ethereal bromine precipitated allylmercuric bromide (m. p. 126°

after crystallisation from alcohol) from the filtered solution. Metallic mercury and unchanged allylmercuric iodide were amongst the other products of the reaction.

Derivatives of Propyne (cf. Hurd, Meinert, and Spence, *J. Amer. Chem. Soc.*, 1930, **52**, 1138; Heilbron, Jones, and Weedon, *J.*, 1945, 81).—Purified acetylene was passed for 2 hours into a solution of sodamide, prepared from sodium (35 g.) and liquid ammonia (500 c.c.), at a rate of 3 l./min. and the sodium acetylide converted into propyne by addition of methyl iodide (210 g.), the mixture being kept at −40°. The gas was purified by passage through water, 10% sulphuric acid and a calcium chloride tower, Bunsen non-return valves being fitted between the various parts of the apparatus, and finally led into a vigorously stirred solution of ethylmagnesium bromide prepared from ethyl bromide (109 g., 1 mol.). The latter was contained in a 1½-l. flask fitted with a gas-inlet tube, a mercury-seal stirrer, and a liquid-ammonia condenser (Vaughn and Poggi, *J. Chem. Educ.*, 1931, **8**, 2433), the whole being cooled to −40°. The ammonia condenser was replaced by one of the ordinary type and the liquid allowed gradually to warm to room temperature. Mercuric chloride (160 g.) was then added in small portions, and the product isolated in the usual manner. This material was extracted, by means of a Soxhlet extractor, with acetone (3 × 100 c.c.). *Prop*-1-*ynylmercuric chloride* separated from the acetone in glistening plates and recrystallised from methyl alcohol as feathery plates, m. p. 135—136° (Found: Cl, 13·7; Hg, 73·1. C_3H_3ClHg requires Cl, 12·9; Hg, 72·9%). Owing to the high mercury content it was impossible to obtain satisfactory analysis figures for carbon and hydrogen. Treatment with potassium cyanide solution afforded dipropynylmercury, separating from methyl alcohol or toluene in colourless glistening plates, m. p. 203—204° (Found: C, 26·5; H, 2·4; Hg, 72·7. Calc. for C_6H_6Hg: C, 25·9; H, 2·2; Hg, 71·9%). Its identity was confirmed (m. p. and mixed m. p.) by comparison with a sample prepared from alkaline mercuric iodide and alcoholic propyne obtained by the dehydrohalogenation of propylene bromide (Johnson and McEwen, *J. Amer. Chem. Soc.*, 1926, **48**, 472). Neither propynylmercuric chloride nor the dipropynyl compound could be reduced at ordinary temperatures. Platinum oxide catalyst used under high pressures and temperature appeared to yield propyne.

Propylene Derivatives.—Ethylmercuric bromide, prepared by boiling under reflux ethylmagnesium bromide (from 55 g. of ethyl bromide) with mercuric bromide for 1½ hours in an atmosphere of nitrogen, separated from ethyl alcohol in shining leaflets m. p. 193° (140 g., 90%).

Ethylmercuric bromide (50 g., 0·5 equiv.) was added in small portions to allylmagnesium bromide (Gilman and McGlumphy, *Bull. Soc. chim.*, 1928, **43**, 1322) prepared from allyl bromide (40 g.). The temperature was kept below 5° and vigorous stirring was important. When solution of the solid was complete, the product was decomposed with ice and 1% sulphuric acid, and the organic mercury compound extracted with ether and dried (Na_2SO_4). Removal of the solvent in a vacuum left a fawn-coloured residual liquid which was washed with absolute alcohol and kept in a vacuum-desiccator. *Allylethylmercury* (Found: Hg, 73·1, 73·5. $C_5H_{10}Hg$ requires Hg, 74·0%) decomposed when distilled, even in the presence of dry oxygen-free nitrogen, the products being diallylmercury (isolated as diallyl and mercury) and diethylmercury, b. p. 152—155° (Found: Hg, 77·8. Calc. for $C_4H_{10}Hg$: Hg, 77·9%). Allylethylmercury decomposes at room temperature also, as indicated by the formation of a grey mist of mercury. The highest yield was 60% and was obtainable only when the scale of the preparation was small. Attempts to prepare the compound from allylmercuric iodide and ethylmagnesium iodide led to the formation of ethylmercuric iodide and diethylmercury. In a second experiment allylmercuric bromide (8 g.) was added to ethereal diethylzinc (1·5 g.; *Org. Synth.*, Coll. Vol. II, p. 184). Reaction was immediate and solution took place accompanied by the formation of a mist of mercury, together with diethylmercury and diallyl.

Reactions of Allylethylmercury.—The liquid (1·5 g.) was dissolved in ether, and a saturated alcoholic solution of mercuric chloride was added to the boiling solution until precipitation was complete. Fractional crystallisation of the precipitate from alcohol afforded ethylmercuric chloride, m. p. 190—191° (55%), the more soluble allylmercuric chloride (45%), m. p. 110—112°, being obtained from the mother-liquors. An ethereal solution of allylethylmercury (2 g.) likewise yielded ethylmercuric chloride (70%) when warmed with alcohol (7 c.c.) saturated with hydrogen chloride. Addition of potassium iodide precipitated the remainder of the mercury as mercuric iodide.

Boron compounds.

Methyl borate (Etridge and Sugden, *J.*, 1928, 989) was fractionally distilled and freed from the last traces of methyl alcohol by concentrated sulphuric acid (Seaman and Johnson, *J. Amer. Chem. Soc.*, 1931, **53**, 713). *n*-Butyl borate was obtained by the method of *Org. Synth.* (Coll. Vol. II, p. 106) (Found: B, 4·6, 4·6. Calc. for $C_{12}H_{27}O_3B$: B, 4·8%). Triallyl borate (Councler, *loc. cit.*), b. p. 77—78°/14 mm. (yield 84%) (Found: B, 6·0; 5·8. Calc. for $C_9H_{15}O_3B$: B, 6·0%), and trimethallyl borate (Thomas, *J.*, 1946, 820, see also Ballard, B.P. 595,502/1947), b. p. 119—121°/20 mm. (yield, 87%) (Found: B, 4·9, 5·1. Calc. for $C_{12}H_{21}O_3B$: B, 4·9%), were prepared by the latter author's method of slowly distilling a mixture of boric acid, benzene, and the appropriate alcohol until no more water came over.

Derivatives of Diallylboric Acid.—Boron trifluoride was prepared from potassium fluoroborate (52 g.), boron oxide (8 g.), and concentrated sulphuric acid (100 c.c.) in all-glass apparatus (Booth, *Inorg. Synth.*, **1**, 21). A slow stream of the gas was passed into a stirred ethereal solution of allylmagnesium bromide obtained from allyl bromide (80 g.), magnesium (48 g.), and ether (800 c.c.), which was cooled to −10°. After 1 hour, the product was decomposed at 0° with saturated ammonium chloride solution, and the ethereal layer was siphoned into a nitrogen-filled separating funnel. The aqueous layer was extracted with ether, and the combined extracts were dried (Na_2SO_4). Removal of the solvent in nitrogen afforded a faintly yellow liquid containing a small amount of inorganic material. Fractionation gave products, b. p. 90°/12 mm., 120°/12 mm., and 95°/0·2 mm., all colourless liquids with garlic odours, unsaturated to bromine water and alkaline potassium permanganate, and free from fluorine. They had nearly identical compositions (Found, respectively: C, 68·1; H, 9·9%; *M*, 356. C, 68·3; H, 10·0. C, 68·6; H, 10·9%; *M*, 403). The high molecular weights may be connected with the well-known tendency of boron oxides to form polymeric cyclic products in contact with boron trifluoride. The same substances were formed when boron trifluoride–ether complex was substituted for gaseous boron trifluoride. Repeated distillation of the two lower-boiling fractions led to dehydration and the formation of pure *bisdiallylboron oxide*, b. p. 118—120° mm. (32%) (Found: C, 71·0; H, 9·9; B, 10·6. $C_{12}H_{20}OB_2$ requires C, 71·2; H, 9·9; B, 10·9%).

Methyl Diallylborate.—A three-necked flask (2 l.) was fitted with a stirrer, a nitrogen-inlet concentric with its shaft, and a dropping funnel with its delivery tube bent towards the centre of the flask. The third neck carried a Y-shaped nitrogen outlet, one arm of which was connected to the dropping funnel and the other to a reflux condenser. The flask was cooled to −15° and the air displaced by the passage, for 20 minutes, of a rapid stream of oxygen-free nitrogen. A solution of methyl borate (44 g.) in ether (200 c.c.) was rapidly introduced into the flask, and previously prepared ethereal allylmagnesium bromide (from 60 g., 0·5 mol. of allyl bromide) siphoned under nitrogen into the dropping funnel. The addition of the magnesium compound caused the precipitation of a thick white addition product which, after overnight stirring in an atmosphere of nitrogen, was decomposed and extracted with ether in the usual way and dried. Distillation of the ether from a steam-bath led to partial crystallisation; water (20 c.c.) was therefore added and the distillation continued until no more volatile products were obtained. The fawn-coloured liquid residue was separated from precipitated boric acid and on distillation yielded three main fractions: (i) B. p. 82°/15 mm. (31%), *methyl diallylborate*, unchanged by repeated distillation (Found: C, 67·8, 67·9; H, 9·9, 10·2; B, 8·7. $C_7H_{13}OB$ requires C, 67·8; H, 10·4; B, 8·8%). Bisdiallylboron oxide was obtained when the ester was hydrolysed and the product distilled. (ii) B. p. 110°/0·4 mm., which, like the first fraction, was unsaturated and was probably not a methyl ester since it was also obtained from tributyl borate (below). When it was boiled with water boric acid was the sole product but the high boiling point indicated that it may have been *diallyl allylborate* (Found: C, 62·4; H, 9·6; B, 6·2. $C_9H_{15}O_2$ requires C, 65·0; H, 9·0; B, 6·6%). It may be remarked that analyses of boron compounds for carbon present great difficulty and low results are often met with in the literature; this has been attributed to the fusion of boron trioxide with the carbon particles. (iii) The third fraction, b.p. >250°/0·2 mm., was not investigated.

Substitution of triallyl borate for the methyl ester yielded a liquid, b. p. 75—76°/11 mm., which appeared to be mainly unchanged ester. Allyl alcohol was also formed. Use of tri-*n*-butyl borate led to a small amount of a colourless viscous oil, b. p. 111°/0·1 mm., insoluble in water but soluble in alkali. Analysis indicated its *possible* identity with (ii) described above (Found: C, 62·0; H, 8·7; B, 5·0%). The quantity was too small for extensive attempts to determine its structure and no method for obtaining it in larger amounts was successful.

*Reaction of Allylmagnesium Bromide with Di-*n*-butylboron Bromide.*—In the apparatus previously described, allylmagnesium bromide (1 equiv.) was treated with di-*n*-butylboron bromide (14 g.; Johnson, Snyder, and Van Campen, *loc. cit.*). The products were tri-*n*-butylborine, b. p. 86°/20 mm. (8 g.) (Found: B, 5·9. Calc. for $C_{12}H_{27}B$: B, 6·0%), and bisdiallylboron oxide (2 g.) (Found: C, 70·9; H, 9·7. Calc. for $C_{12}H_{20}OB_2$: C, 71·2; H, 9·9%).

Reactions with Diethylzinc.—The reagent, purified by distillation in carbon dioxide, had b. p. 117—119°.

(*a*) *In tetralin.* A solution of triallyl borate (20 g., 1 equiv.) in purified tetralin (20 g.) was slowly added to a vigorously stirred mixture of diethylzinc (41 g., 3 equivs.) and tetralin (40 g.), carbon dioxide being passed through the liquid. Little reaction occurred at 0° and the flask was heated at 100° for 2 hours. Fractionation of the product afforded fractions, (i) b. p. 85—95° (2 g.), and (ii) b. p. 130—140° (8 g.). Both these liquids had a pronounced phenolic odour, contained combined boron, and were unsaturated. The lower-boiling reacted vigorously with sodium but no indication of free allyl alcohol was obtained. These substances were insoluble in water but dissolved in sodium hydroxide, the second fraction with evolution of heat. Fraction (i) gave analytical figures corresponding to the diethyl ethylborate (b. p. 125°) though its b. p. was nearer to that of ethyl diethylborate (Found : C, 55·3; H, 11·5; B, 7·8. Calc. for $C_6H_{15}O_2B$: C, 55·4; H, 11·5; B, 8·5%). However, its stability to water was greater than that of either of these two esters. Fraction (ii) was probably, in spite of the low analysis for carbon, *allyl diethylborate* (Found : C, 64·0; H, 11·8; B, 8·3. $C_7H_{15}OB$ requires C, 66·6; H, 11·9; B, 8·7%). Hydrolysis with sodium hydroxide followed by acidification yielded a saturated acid which on distillation furnished bisdiethylboron oxide, b. p. 143° (Meerwein and Sönke, *J. pr. Chem.*, 1936, **147**, 251).

(*b*) The experiment was repeated in the absence of a solvent (Councler, *loc. cit.*). A colourless liquid, b. p. 115—120°, was isolated (Found : B, 7·8. $C_8H_{15}OB$ requires B, 7·9%). The figure for boron, in conjunction with Councler's analytical figures for carbon and hydrogen, indicate the substance to be *ethyl diallylborate.*

(*c*) Experiment (*a*) was repeated with trimethallyl borate (32 g.) in tetralin (30 g.), and diethylzinc (53 g.) in the same solvent (20 g.). A large part of the methallyl alcohol (20 g.) was recovered unchanged, together with a liquid, b. p. 52—54°/17 mm. (3 g.), which appeared to be *methallyl diethylborate,* though the analytical value for hydrogen was not altogether satisfactory (Found : C, 68·9; H, 13·1; B, 7·5. $C_8H_{17}OB$ requires C, 68·5; H, 12·1; B, 7·8%).

Di-n-*butyl 3-methoxypropylborate* was prepared by addition of tri-*n*-butyl borate to one equivalent of the Grignard reagent prepared from 3-methoxypropyl chloride (Noyes, *Amer. Chem. J.*, 1897, **19**, 767; Palomaa and Jansen, *Ber.*, 1931, **64**, 797; 1938, **71**, 597). It had b. p. 140—150°/41 mm., the yield being 20% (Found : C, 62·2; H, 12·1; B, 4·9. $C_{10}H_{27}O_3B$ requires C, 62·6; H, 11·7; B, 4·8%).

Nearly all the analyses, except for those for mercury and boron, were carried out by Drs. Weiler and Strauss, Oxford. The Department of Scientific and Industrial Research is thanked for a grant in aid of this research.

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