times as potent as VII in the Clauberg test without eliciting the narcotic effect of the latter. The oral activity generally decreases by more than seven - membered straight chains. Comparable findings on enol ethers of the above cited ketones variously substituted soon will be reported elsewhere.

These novel compounds were obtained: (A) with orthoformic esters in the conventional manner[10]; (B) by treating Δ^4-3-ketones and alcohols with isoöctane as azeotropic carrier[11]; (C) by acid-catalyzed interchange reaction[12] between the chosen alcohol and a preformed (mostly ethyl) enol ether generally obtained with (A) procedure; (D) by the same way without isolation of firstly formed ether; (E) by converting in proper conditions the as above obtained enol ethers to the desired compounds by reduction, acylation, saponification or condensation reactions.

[10] A. Serini and H. Köster, *Ber.*, **71**, 1766 (1938).

[11] A. Ercoli and P. de Ruggieri, U. S. Patent 2,835,667 (May 20, 1958). Senior author wishes to thank Dr. P. de Ruggieri (Ormonoterapia Richter, Milano) for his effective collaboration in developing method B.

[12] A. Ercoli, German Patent 1,068,256 (published November 5, 1959).

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THE PREPARATION OF *t*-BUTYLDIALKYLBORANES AND 1-*t*-BUTYLBOROCYCLOPENTANE FROM OLEFINS AND TRIMETHYLAMINE *t*-BUTYLBORANE

Sir:

Recent interest in the preparation of mixed trialkylboranes[1,2] and 1-alkylborocyclopentanes[3] prompts us to report a new method for the preparation of these compounds.

Trimethylamine *t*-butylborane,[4] which is prepared by the lithium aluminum hydride reduction of *t*-butylboroxine in the presence of trimethylamine, has been found to add to olefins at 50–60° at an extremely rapid rate. The great rates of these reactions are in sharp contrast to those observed with pyridine borane[5] and trimethylamine borane[6] since the latter reactions required higher temperatures and longer reaction times. This rate difference is attributed to the greater rate of dissociation of the *t*-butylborane amine complex.

The addition of ethylene, propylene, 1-butene and *i*-butene to 0.10 mole quantities of trimethyl amine *t*-butylborane at atmospheric pressure and 50–60° was complete after 1–2 hours. Trimethylamine was evolved during the reaction. Vacuum distillation of the products afforded the corresponding *t*-butyl dialkylboranes in up to 90% yield. Similar treatment of 1,3-butadiene and isoprene afforded 1-*t*-butyl borocyclopentane and 1-*t*-butyl-3-methylborocyclopentane, respectively. Structures were assigned on the basis of C, H and B analyses, infrared spectra and H^1n.m.r. spectra. The *t*-butyl-di-isobutylborane obtained in this work gave a H^1n.m.r. spectrum identical to that obtained by Davies, *et al.*,[2] with the exception of the absence of the small band which these authors attributed to restricted rotation.

Dimethyldivinylsilane reacted smoothly with trimethylamine *t*-butylborane to produce 1-boro-1-*t*-butyl-4,4-dimethyl-4-silacyclohexane, a novel heterocycle which contains a boron atom and a silicon atom in a six-membered ring. The table records representative data.

CHARACTERISTICS OF MIXED BORANES

Borane	B.p. °C. (mm.)	Yield, %
t-Butyl diethyl	60 (70)	35
t-Butyl di-(1-propyl)	67 (22)	88
t-Butyl di-(1-butyl)	74 (6.1)	90
t-Butyl di-(*i*-butyl)	62 (7.5)	85
1-*t*-Butyl borocyclopentane	55 (55)	60
1-*t*-Butyl-3-methyl borocylopentane	67 (54)	55
1-Boro-1-*t*-butyl-4,4-dimethyl-4-silacyclohexane	44 (2)	58

Further work with other trimethylamine alkylborane reactions is in progress and will be reported at a later date.

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[1] G. F. Hennion, P. A. McCusker and A. J. Rutkowski, THIS JOURNAL, **80**, 617 (1958).

[2] A. G. Davies, D. G. Hare and R. F. M. White, *Chem. Ind.*, 1315 (1959).

[3] R. Koster, *Angew. Chem.*, 520 (1959).

[4] M. F. Hawthorne, THIS JOURNAL, **81**, 5836 (1959).

[5] M. F. Hawthorne, *J. Org. Chem.*, **23**, 1788 (1958).

[6] E. C. Ashby, THIS JOURNAL, **81**, 4791 (1959).

A SIMPLE PREPARATION OF DIALKYL ALKYLTHIOBORONATES AND TRIALKYLTHIOBORATES

Sir:

Trimethylamine alkylboranes, prepared from the corresponding alkylboroxines by lithium aluminum hydride reduction in the presence of trimethylamine,[1] and alkylthiols react at 60–100° to produce the corresponding dialkyl alkylthioboronates in moderate yields.

$$RB^{-}H_2—N^{+}(CH_3)_3 + 2R'SH \longrightarrow 2H_2 + N(CH_3)_3 + RB(SR')_2$$

The use of trimethylamine borane with high boiling thiols affords the corresponding trialkylthioborates. Both types of reaction appear to be general and constitute simple routes to previously unavailable compounds.

Dialkyl alkylthioboronates and trialkylthioborates are hydrolyzed easily by water to the corresponding thiol, alkylboronic acid and boric acid, respectively. The dialkyl alkylthioboronates did not disproportionate appreciably during distillation at temperatures up to 150°. The table presents representative data. Analytical values obtained for C, H and B were satisfactory.

Treatment of di-*n*-amyl-*n*-butyl thioboronate and the corresponding *t*-butyl compound with excess mercuric chloride in toluene at 80° produced the corresponding alkyl boron dichlorides in 60% yield. The formation of the Hg–S bond may provide driving-force for other similar reactions.

$$RB(SR')_2 + 2\ HgCl_2 \longrightarrow RBCl_2 + 2\ ClHgSR'$$

Further work is in progress and will be reported at a later date.

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[1] M. F. Hawthorne, THIS JOURNAL, **81**, 5836 (1959).

CHARACTERISTICS OF DIALKYL ALKYLTHIOBORONATES AND TRIALKYLBORATES

Compound	Yield, %	B.p. (mm.), °C.
Ethylene *n*-butyl thioboronate	45	84 (6)
Ethylene *i*-butyl thioboronate	38	83 (6.5)
Di-*n*-amyl-*n*-butyl thioboronate	29	132 (0.5)
Di-*n*-amyl-*t*-butyl thioboronate	72	122 (0.2)
Di-*n*-butyl-*s*-butyl thioboronate	63	105 (0.8)
Di-*n*-butyl-*n*-hexyl thioboronate	58	119 (0.3)
Tri-*n*-amyl thioborate	65	164 (0.4)
Tri-*n*-butyl thioborate	70	147 (1.0)

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A NEW METHOD FOR THE PREPARATION OF CRYSTALLINE POLYVINYL CHLORIDE

Sir:

We have prepared crystalline polyvinyl chloride with conventional free-radical catalysts at 50° using aliphatic aldehydes as polymerization media. Although all aliphatic aldehydes tried have produced this stereoregulating effect, *n*-butyraldehyde and 2-ethylhexylaldehyde appear to give the best results. As is to be expected from the chain transfer activity of aldehydes, very low molecular weight polymers are produced, *e.g.*, approximately 5,000. The reaction is carried out at 50° using a mole to mole ratio of monomer to aldehyde and a millimole of free-radical catalyst per mole of monomer. A typical polymerization using 72.0 g. of *n*-butyraldehyde, 62.5 g. of vinyl chloride, and 0.16 g. of azodiisobutyronitrile in 9 hours yields 9.13 g. of polyvinyl chloride. The crystalline material in tetrahydrofuran gives a cloudy solution which does not clear up on heating. The same effect is noted with cyclohexanone but on heating to 120° the solution becomes clear.

The crystallinity, and hence stereoregularity, of the polymers was investigated using X-ray diffraction and infrared absorption methods. The regular sequences in polyvinyl chloride crystallize readily so that changes in crystallinity are directly related to changes in regularity. The unoriented X-ray pattern of the polyvinyl chloride prepared in *n*-butyraldehyde possesses sharp lines with "d" spacings at 5.16 (m), 4.66 (s), 3.65 (m), 3.44 (m), 2.84 (m), 2.56 (w), 2.28 (m), 2.07 (w), 1.78 (vw), 1.59 (vw), 1.40 (vw), 1.25 (vw), 1.14 (vw) Å. (letters in parentheses indicate relative intensities where s = strong, m = medium, w = weak, vw = very weak). These values agree well with those reported by Fordham, Burleigh and Sturm.[1] The lines with "d" spacings at 3.65, 1.40, 1.25, and 1.14 Å., however, have not been reported previously.

With regard to the infrared absorption spectrum of polyvinyl chloride, the ratio of the absorbance at 635 cm.$^{-1}$ to that at 692 cm.$^{-1}$ has been used as a measure of crystalline syndiotactic units in the polymer.[2-6] Table I gives the D_{635}/D_{692} ratio for polyvinyl chloride prepared in bulk at high and low temperatures and in *n*-butyraldehyde at high temperature.

TABLE I

INFRARED ABSORPTION DATA

Polyvinyl Chloride Prepared in	D_{635}/D_{692}
Bulk at +50°	1.5
Bulk at −70°	2.6
n-Butyraldehyde at +50°	4.3

An increase in the absorbance ratio is indicative of increased crystallinity. The infrared absorption measurements were made using films cast on potassium bromide discs from tetrahydrofuran or cyclohexanone solutions; for the polymer prepared in *n*-butyraldehyde the film was cast from a cyclohexanone solution at 120°. Based on the above evidence, we have assigned the syndiotactic structure to this polyvinyl chloride.

The stereoregulating effect of aliphatic aldehydes on the free-radical polymerization of vinyl chloride is not yet understood. Study of the mechanism of this effect is in progress.

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[1] J. W. L. Fordham, P. H. Burleigh, and C. L. Sturm, Abstracts 135th A.C.S. Meeting, Boston, April, 1959.

[2] S. Mizushima, T. Shimanouchi, K. Nakamura, M. Hayashi, and S. Tsuchiya, *J. Chem. Phys.*, **26**, 970 (1957).

[3] R. J. Grisenthwaite and R. F. Hunter, *Chem. & Ind.*, 433 (1959).

[4] S. Krimm, A. R. Berens, V. L. Folt and J. J. Shipman, *ibid.*, 433 (1959).

[5] T. Shimanouchi, S. Tsuchiya and S. Mizushima, *J. Chem. Phys.*, **30**, 1365 (1959).

[6] S. Krimm, *Society of Plastic Engineers Journal*, (Sept.) 797 (1959).

A NOVEL SYNTHESIS OF BENZOCYCLOBUTENE DERIVATIVES[1]

Sir:

About a year ago we reported[2] the formation of a stable dipositive carbonium ion from trichloromethylpentamethylbenzene (I). We now wish to record another unusual and useful reaction of this and related substances.

I is a colorless, crystalline solid, m.p. 94.5–95.0°. It was observed that at or slightly above its melting point, *I evolved hydrogen chloride.* In a quantitative experiment, 1.074 g. (4.05 mmoles) of I was heated at 110–125° in a dry nitrogen stream which subsequently passed through standard sodium hydroxide. In the first hour, 3.76 mmoles of hydrogen chloride was collected. Two more hours netted 0.50 mmole, and after three additional hours, only 0.03 mmole more of hydrogen chloride was produced (a total of 105.9% of the theoretical for one mole). On cooling, there was isolated a crystalline solid II, m.p. 73–74° (from pentane). *Anal.*[3] Calcd. for $C_{12}H_{14}Cl_2$:

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, under grant 488-C.

[2] H. Hart and R. W. Fish, THIS JOURNAL, **80**, 5894 (1958). A detailed report of this work is in preparation.

[3] All analyses by Spang Microanalytical Laboratory, P. O. Box 1111, Ann Arbor, Michigan.