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).

VISTER RESEARCH LABORATORIES ALBERTO ERCOLI
CASATENOVO (COMO), ITALY RINALDO GARDI

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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.

(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).

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.

ROHM & HAAS COMPANY
REDSTONE ARSENAL RESEARCH DIV.
HUNTSVILLE, ALABAMA M. FREDERICK HAWTHORNE

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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.

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