CONCLUSIONS

1. It was shown that N-carbethoxy-bis(trifluoromethyl)phenyliminoaziridine is formed during nucleophilic epimination of the anil of bis(trifluoromethyl)ketene with p-nitrobenzenesulfonyloxyurethane. A scheme of its isomerization to 2-ethoxy-4-phenylimino-5,5-bis(trifluoromethyl)-2-oxazoline was established.

2. The reaction of bis(trifluoromethyl)ketene anil with N-chloroamides yielded N-phenyl-N'-acyl α -chlorohexafluoroisobutyric acid amidines.

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ORGANOBORON COMPOUNDS.

346. ADDITION OF ALLYL (ALKYL) BORANES TO CARBONYL COMPOUNDS

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After we have developed the preparative methods for the preparation of mixed allyl(alkyl)boranes [1-4], we started a systematic study of the chemical properties of this class of compounds and their possible utilization in organic synthesis. In [3], we described the irreversible allyl rearrangement and the splitting of the boron-allyl bonds under the action of water and alcohols.

In the present work, we studied the reactions of allyl(dialkyl)boranes or triallylborane with carbonyl compounds, leading to unsaturated esters of organoboric acids and allyl carbinols.

The direction of the reactions of the organic boron derivatives with aldehydes and ketones is determined by the nature of the radical attached to the boron atom, structure of the carbonyl compound, and the conditions of the process. Alkyl- and arylboranes do not add to the double bond of the C=O group, except in the reaction of trialkylboranes R₃B with monomeric CH₂O, which in the presence of atmospheric oxygen leads to compounds R₂BOCH₂R [5]. When heated above 100°C, aromatic aldehydes are quantitatively reduced by trialkylboranes to the corresponding alcohols [6-8]. The reaction is accompanied by the elimination of the olefinic hydrocarbon, and had been used for the synthesis of pure α -olefins [6, 7] and counterthermodynamic isomerization of methylcyclenes into methylenecyclanes [6].

Aliphatic aldehydes and ketones react with triphenyl- and tribenzylboranes at $145-170^{\circ}C$, mainly with the formation of ethers of type $RCH=CR'-OBR_2$ (I) [9]. In the presence of pivalic acid as catalyst, vinyloxyboranes (I) are readily obtained at $80-100^{\circ}C$ from trialkylboranes also [10], while triethylborane converts many cycloalkanones and acyclic ketones into dimeric and trimeric products of crotonic condensation [11]. Triallylborane [12] and other allylboranes [12-15] react with aldehydes and ketones, including ketones of the steroids class

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1892-1896, August, 1978. Original article submitted April 1, 1977. [16] in the same way as organomagnesium compounds, by the addition of the boron-allyl fragment to the double bond of the C=O group, which is due, first, to the lower energy of the B-C bond in these compounds, and second, their ability to react with an allyl rearrangement in accordance with a six-centered mechanism [13, 15].

We studied the reactions of asymmetric allyl(dialkyl)boranes (II) and diallyl(alkyl)boranes with aldehydes, ketones, and esters, and showed that all these reactions proceed by a scheme of heteroorganic synthesis, and first lead to substituted butenyl esters of the corresponding boric acids. As the result of the reaction of allyl(dialkyl)boranes (II) with aldehydes, taking place with vigorous evolution of heat, unsaturated esters of dialkylboric acids (III) are formed, which on hydrolysis or transesterification by higher alcohols or triethanolamine (TEA) yield 1-substituted butenyl alcohols (IV)



A similar reaction with ketones was used for the synthesis of esters of dialkylboric acids of type (V) and tert alcohols (VI)

(II) + (CH₃)₂CO
$$\xrightarrow{0^{\circ}}$$
 CH₂=CH-CH₂C(CH₃)₂-O-BR₂ $\xrightarrow{\text{TEA}}$ CH₂=CHCH₂C(CH₃)₂OH
(V) (VI)

The boron-allyl fragment is added to the CO group with the allyl rearrangement [13], as demonstrated by the reaction of crotyl(di-n-butyl)borane and acetone



 $R = n - C_4 H_9$

The boric ester (VII) was transesterified without isolation by heating *in vacuo* with triethanolamine (TEA): 1,1,2-trimethyl-3-buten-1-ol (VIII) thus formed was isolated in a yield of 85%.

The reaction of γ, γ -dimethylallyl(di-n-propyl)borane (IX) with butyraldehyde or isovaleraldehyde, followed by treatment with TEA, leads to unsaturated alcohols, 3,3-dimethyl-l-hepten-4-ols (X)



 $R = H, CH_3$

In the IR spectrum of carbinols (X), an intense absorption band of the terminal double bond (1640, 3085 cm⁻¹) is observed. In the PMR spectra of (X, R = H, CH₃), a singlet of the two gem-methyl groups at 0.98 ppm and an ABC spectrum of the terminal double bond protons with δ 4.60-5.09 (2H, CH₂=C) and 5.50-6.20 ppm (1H, CH=) are observed.

Acetylation of alcohols (X) with AcCl in pyridine leads to acetates of 1-hepten-4-ols (XI). It should be noted that compounds of the 1-hepten-4-ol series have a biological activity, and are used as insect attractants [17].

Allyl(dialkyl)- and diallyl(alkyl)boranes readily react with esters, converting them into diallyl(alkyl)carbinols. Thus, the reaction of allyl(di-n-butyl)borane with butyl acetate proceeds at 0°C with vigorous evolution of heat, and yields the butyl ester of di-n-butylboric acid and 4-methyl-1,6-heptadien-4-yl ester of di-n-butylboric acid (XII); transesterification of the latter compound gives 4-methyl-1,6-heptadien-4-ol (XIII) in a yield of 85%:



At the first stage of the reaction, there is an addition of the boron-allyl fragment to the C=O bond with the formation of a boron-containing ketal (XIV), which is unstable and undergoes a β decomposition with the elimination of boric ester and allyl methyl ketone. The latter reacts with the second molecule of allyl(dialkyl)borane to form the ester (XII)



Attempts to isolate the intermediate allyl methyl ketone from the reaction products were unsuccessful. Apparently, this compound is more active with respect to allyl(dialkyl)borane than the starting ester.

The reaction of dially1(n-hexyl)borane with ethyl acetate led to the carbinol (XIII) in a yield of 88%



The tertiary alcohol (XIII) was also obtained in a yield of 70% as the result of the alcoholysis with triethanolamine of the product of the reaction of triallylborane with ethyl acetate.

Esters and other derivatives of higher organic acids react with allyl derivatives of boron similarly to the acetic acid esters. These reactions represent a convenient method for the synthesis of various 4-substituted derivatives of 1,6-heptadiene-4-ols.

The reactions of the allyl derivatives of boron with carbonyl compounds proceed readily and unequivocally under mild conditions, and lead to the corresponding unsaturated alcohols in yields of 80-85%. At the same time, the analogous reactions of allylmagnesium compounds are complicated by side reactions. Therefore, the use of allylboranes has several advantages over Grignard reagents.

EXPERIMENTAL

All the operations with the organoboron compounds were carried out in an atmosphere of dry N_2 or Ar.

The IR spectra were run on the UR-20 spectrometer; the PMR spectra, on Varian DA-60-IL, with hexamethyldisiloxane (HMDS) as the internal standard; the chemical shifts are given with reference to tetramethylsilane (TMS) ($\delta = 0$).

Allyl(diethyl)borane, allyl(di-n-butyl)borane, diallyl(n-hexyl)borane, crotyl(di-n-butyl)borane, and γ,γ -dimethylallyl(di-n-propyl)borane were obtained from the corresponding allyl bromides and esters of alkyl and dialkylboric acids [3, 4].

<u>1-Hexen-4-yl Ester of Diethylboric Acid (III, R = C₂H₅).</u> A 4-ml portion of propionaldehyde was added dropwise at -50°C to 4.5 g of an allyl(diethyl)borane. The reaction proceeded with a vigorous evolution of heat. The mixture was gradually warmed up to $\sim 20^{\circ}$ C. By distillation, 4.25 g (62.5%) of compound (III, R = C₂H₅), bp 68-70°C (20 mm), were isolated. n_D^{23.5} 1.4165. Found (%): C 71.10, H 12.51, B 6.48. C₁₀H₂₁BO. Calculated (%): C 71.50, H 12.54, B 6.44. IR spectrum (ν , cm⁻¹) 1645 and 3080 (CH₂=CH). PMR spectrum (δ , ppm): 0.62-1.70 m (aliphatic protons), 2.0-2.35 t (CH₂C-, J = 6.5 Hz), 3.75-4.2 m (CH), 4.75-5.2 m (CH₂=C), 5.4-6.2 m (CH=).

<u>1-Hexen-4-o1 (allylethylcarbinol) (IV).</u> A 2-ml portion of propionaldehyde was added at -40° C to 4 g of allyl(di-n-butyl)borane (II, R = n-C₄H₉). The mixture was heated to $\sim 20^{\circ}$ C, and then 4 ml of TEA were added. By distillation, 2.2 g (91.5%) of (IV), bp 44-46°C (22 mm), were isolated: n_{D}^{22} 1.4315; compare [12]. IR spectrum (ν , cm⁻¹): 1645, 3080 (CH₂=CH), 3350 (OH).

 $\frac{1,1-\text{Dimethyl-3-buten-1-yl Ester of Diethylboric Acid}{(V, R = C_2H_5)}$ A 1.2-ml portion of acetone was added dropwise to 1.7 g of allyl(diethyl)borane. The mixture warmed up to 80°C. By distillation, 2.15 g (83.5%) of (V, R = C_2H_5), bp 77-78.5°C (30 mm), were isolated; $n_D^{2.4 \cdot 5}$ 1.4191. Found (%): C 70.58, H 12.78, B 6.47. C₁₀H₂₁BO. Calculated (%): C 71.50, H 12.54, B 6.44. IR spectrum (v, cm⁻¹): 1645, 3080 (CH₂=CH). PMR spectrum (δ , ppm): 0.86 s (C₂H₅), 1.3 s (CH₃), 2.3 d (CH₂C, J = 7 Hz), 4.75-5.15 m (CH₂=C), 5.4-6.2 m (CH=).

<u>4-Methyl-1-penten-4-ol (VI).</u> A 2-ml portion of acetone was added to 4.1 g of allyl(din-butyl)borane; the mixture, which warmed up to 80°C, was cooled to $\sim 20^{\circ}$ C, and 4 ml of TEA were added. By distillation, 2.2 g (90.5%) of (VI), bp 36-38°C (45 mm), were obtained; n_D²⁰ 1.4260; compare [12]. IR spectrum (ν , cm⁻¹): 1640, 3080 (CH₂=CH). PMR spectrum (δ , ppm): 1.13 s (CH₃), 2.15 d (CH₂C=, J = 6.5 Hz), 3.7 s (OH), 4.2-5.1 m (CH₂=C), 5.45-6.1 (CH=).

<u>1,1,2-Trimethyl-3-buten-1-ol (VIII).</u> A 5-ml portion of absolute acetone was added at 0-5°C to 4.5 g of crotyl(di-n-butyl)borane, and the temperature of the mixture was brought to ~ 20 °C. In the IR spectrum, a band at 1645 cm⁻¹ appeared. A 5-ml portion of TEA was added to the reaction mixture. By vacuum distillation, 2.3 g (85%) of (VIII), bp 40-42° (14 mm), were obtained. n²_D° 1.4362; compare [18]. IR spectrum (ν , cm⁻¹): 1635, 3080 (CH₂=CH), 3400 (OH). PMR spectrum (δ , ppm): 0.82-1.25 m (CH₃), 2.15 q (CH, J = 7 Hz), 3.55 s (OH), 4.75-5.15 m (CH₂=C), 5.45-6.15 m (CH=).

<u>3,3-Dimethyl-1-hepten-4-o1 (X, R = H).</u> A 3.8-ml portion of butyraldehyde was cautiously added to 9.5 g of γ,γ -dimethylallyl(di-n-propyl)borane (IX). The mixture warmed up spontaneously to 60°C; it was left to stand for 0.5 h at ~ 20 °C, and then 10 ml of triethanolamine were added. By vacuum distillation, 7.35 g (98%) of (X, R = H), bp 77-78°C (19 mm), were obtained: n²₂° 1.4400. Found (%): C 75.53, H 12.95. C₉H₁₈O. Calculated (%): C 75.99, H 12.75. IR spectrum (ν , cm⁻¹): 1640, 3085 (CH₂=CH), 3390 (OH). PMR spectrum (δ , ppm): 0.72-1.72 m (aliphatic protons), 0.98 s (CH₃), 3.00-3.33 m (CH), 3.2 s (OH), 4.58-5.08 (CH₃=C), 5.54-6.07 m (CH=).

3,3-Dimethyl-1-hepten-4-yl Acetate (XI, R = H). A 2-ml portion of acetyl chloride was added to a solution of 3 g of (X, R = H) in 18 ml of absolute pyridine, cooled to -5° C. The temperature was brought up to $\sim 20^{\circ}$ C, and the mixture was stirred for 4 h. The reaction mixture was poured into water with ice (150 ml), and 20 ml of 10% HCl were added. The acetate was extracted with ether, the extract was washed with water to neutral reaction, and dried over Na₂SO₄. The solvent was distilled off. By distillation of the residue, 2.35 g (62%) of the acetate (XI, R = H), bp 77-78°C (15 mm), were obtained; n₂° 1.4305. Found (%): C 71.32, H 11.06. C₁₁H₂₀O₂. Calculated (%): C 71.69, H 10.94. IR spectrum (ν , cm⁻¹): 1640, 3087 (CH₂=CH), 1740 (C=O), PMR spectrum (δ , ppm): 0.72-1.70 m (aliphatic protons), 0.98 s (CH₃), 3.97 t (CH, J = 6 Hz), 4.57-5.10 m (CH₂=C), 5.53-6.03 m (CH=).

3,3,6-Trimethyl-1-hepten-4-ol (X, R = CH₃). A 4-ml portion of isovaleraldehyde was added at -20-10°C to 4.9 g of (IX). The temperature of the mixture was brought up to $\sim 20^{\circ}$ C. The mixture was then heated to 70°C, left to stand for 10 min at this temperature, and 8 ml of triethanolamine were added. The compound was distilled at 58-70°C (13 mm). Repeated distillation yielded 3 g (65%) of (X, R = CH₃), bp 62-64°C (13 mm); n_D²° 1.4438. Found (%):

C 75.90; H 12.99. $C_{10}H_{20}O$. Calculated (%): C 76.86, H 12.90. IR spectrum (ν , cm⁻¹): 1640, 3085 (CH₂=CH), 3430 (OH). PMR spectrum (δ , ppm): 0.63-1.76 m (aliphatic protons), 0.98 s (CH₃), 3.07-3.47 (OCH), 3.57 s (OH), 4.69-5.09 m (CH₂=C); 5.62-6.07 m (CH=).

<u>3,3,6-Trimethyl-1-hepten-4-yl Acetate (XI, R = CH₃).</u> A 1-ml portion of acetyl chloride was added, with cooling (-5-0°C), to a solution of 8.8 g of (X, R = CH₃) in 15 ml of pyridine. The temperature was brought up to ~ 20 °C, and the mixture was left to stand for 4 h. The reaction mixture was poured into 100 ml of water with ice and 10 ml of 10% HCl were added. The acetate was extracted with ether, and the extract dried over Na₂SO₄. The solvent was distilled off. By distillation of the residue, 3 g (85%) of (XI, R = CH₃), bp 80-82°C (15 mm), were obtained; n₂° 1.4294. Found (%): C 72.63, H 11.30. C₁₂H₂₂O₂. Calculated (%): C 72.68, H 11.18. IR spectrum (ν , cm⁻¹): 1638, 3090 (CH₂=CH), 1740 (C=0). PMR spectrum (δ , ppm): 0.67-1.55 m (aliphatic protons), 0.98 s (CH₃), 1.95 s (CH₃C=O), 3.98 t (CH, J = 6 Hz), 4.59-5.11 m (CH₂=C), 5.53-6.06 m (CH=).

<u>1,1-Diallylethyl Ester of Di-n-butylboric Acid (XII, R = n-C₄H₉).</u> A 5.2-g portion of butyl acetate was added at -40°C to 6.2 g of allyl(di-n-butyl)borane, and the mixture was heated to 20°C (in the IR spectrum, bands in the 1700-1725-cm⁻¹ region, characteristic of dialkyl ketones, are absent, but there is an intense band at 1745 cm⁻¹). Then, another 6.2 g of allyl(di-n-butyl)borane were added; the temperature spontaneously rose to 40°C. By vacuum distillation. 7 g (94%) of butyl ester of dibutylboric acid, bp 66-68°C (3 mm), were isolated: n_D^{20} 1.4228 and 4.6 g (50%) of ester (XII), bp 86-87°C (3 mm); n_D^{21} 1.4410.

In the IR spectrum of compound (XII), bands at 1645 and 3080 cm⁻¹ (CH₂=CH) were observed.

PMR spectrum (δ , ppm): 0.62-1.75 m (aliphatic protons), 2.30 d (4H, CH₂C=, J = 6.5 Hz), 4.60-5.15 m (4H, CH₂=C), 5.45-6.20 (2H, CH=).

<u>4-Methyl-1,6-heptadien-4-ol (XIII).</u> a) When a mixture of 4.6 g of the ester (XII) and 3 ml of TEA were heated in the Favorski flask with simultaneous distillation, 2.15 g (93%) of compound (XIII), bp 48-50°C (12 mm), were obtained; $n_D^{22.5}$ 1.4497; compare [19]. IR spectrum (v, cm⁻¹): 1645 and 3080 (CH₂=CH). PMR spectrum (δ , ppm): 1.1 s (CH₃), 2.2 d (CH₂C=, J = 7 Hz), 3.05 s (OH), 4.65-5.15 m (CH₂=), 5.45-6.25 m (CH=).

b) A 4.7-ml portion of ethyl acetate was added to 5.3 g of allyl(diethyl)borane cooled to -30° C. The temperature spontaneously rose to 60°C. The mixture was cooled to 20°C, and 6.4 ml of TEA were added. By distillation, 2.3 g (76.5%) of carbinol (XIII), bp 62-63°C (23 mm), were obtained; n_{D}^{2} 1.4502.

c) The reaction of 7.2 g of dially1(n-hexyl)borane with 4 ml of ethyl acetate, followed by treatment with 5.5 ml of TEA, yielded 2.25 g (88%) of carbinol (XIII), bp 64-65°C (24 mm); n_D^{23} 1.4490.

d) Similarly, from 8.7 g of triallylborane, 8.6 g of ethyl acetate and 20 ml of TEA, 5.6 g (70%) of carbinol (XIII), bp 63-64°C (23 mm), were obtained; $n_D^{21.5}$ 1.4509.

CONCLUSIONS

1. Allyl(dialkyl)boranes and diallyl(alkyl)boranes react with carbonyl compounds by the addition of the boron-allyl fragment to the double bond of the C=O group (according to the scheme of heteroorganic synthesis). The addition proceeds with the allyl rearrangement.

2. The reaction of allylboranes with aldehydes, ketones, and esters, followed by hydrolysis or transesterification of the unsaturated esters of boric acids thus formed, is a convenient method for the synthesis of 1-substituted 3-butenols and dienic alcohols.

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