Tetrahedron Letters No.19, pp. 1147-1150, 1964. Pergamon Press Ltd.
Printed in Great Britain.

THE CLEAVAGE OF CARBON-CARBON BOND IN THE DERIVATIVES OF BARENECARBOXYLIC ACIDS UNDER THE ACTION OF BASES

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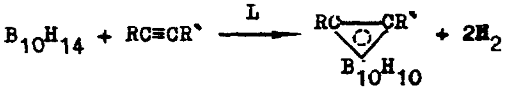
(Received 30 March 1964)

We recently reported(1) together with V.I.Stanko, V.A. Bratzev and O.Yu.Ckhlobystin the synthesis of a novel class of organoboranes $B_{10}H_{10}C_2RR'$ by the reaction of acetylenic compounds with decaborane in the presence of substances forming the diligand derivatives $B_{10}H_{12}L_2$:



$$B_{10}H_{14} + RC{\equiv}CR' \xrightarrow{L} \underset{B_{10}H_{10}}{RC{-}CR'} + 2H_2$$

L= CH_3CN, $(C_2H_5)_3As$, $(C_2H_5)_2S$, $HCON(CH_3)_2$, etc.

For the parent compound $B_{10}H_{10}C_2H_2$ prepared from acetylene and decaborane by above reaction it has been proposed the trivial name <u>barene</u> (for $B_{10}H_{10}C_2H$ radical - <u>barenyl</u>).Barene and its derivatives exhibit a high oxidative, thermal and hydrolytic stability[a].These organoborane it appears enter into a more general group of compounds of empirical formula $B_nH_nC_2H_2$ named carboranes(6).

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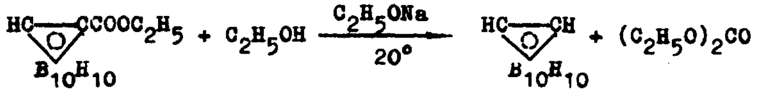
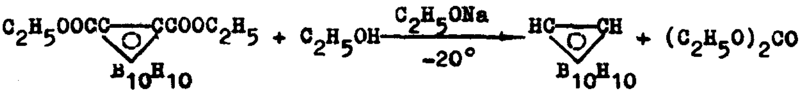
[a] About the reactions and structure of barene and its derivatives it was reported elsewhere(2,3,4,5).

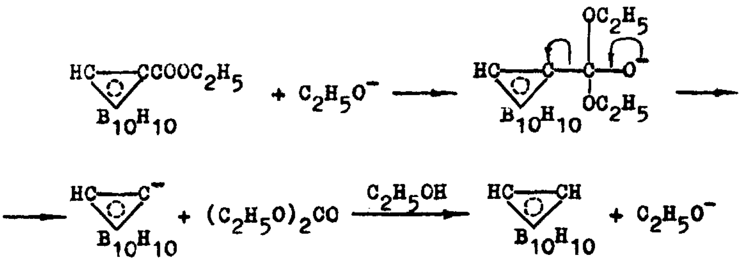
In this paper we report some examples of unusual easy cleavage of carbon-carbon bond in the derivatives of barenecarboxylic acids under the action of bases such as sodium etoxyde and lithium aluminium hydride. We have found that by the action of catalytic amounts of sodium ethoxyde on ethyl barenecarboxylate (m.p. 61-62°. Calcd. for $B_{10}C_5H_{16}O_2$: C, 27.64; H, 7.69; B, 49.77. Found: C, 27.62; H, 7.88; B, 49.21) in the ethanolic solution at room temperature proceeds smoothly the alcoholysis of carbon-carbon bond between the carbon atom of barene nucleus and carbon atom of carbethoxy group with the formation of barene and diethyl carbonate:



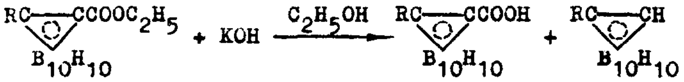
Likewise the alcoholysis of carbon-carbon bond in diethyl barenedicarboxylate (m.p. 10-11°. Calcd. for $B_{10}C_8H_{20}O_4$: C, 33.34; H, 6.95; B, 37.50; Found: C, 33.26; H, 6.95; B, 38.55) proceeds to form barene and diethyl carbonate:



The easy cleavage of carbon-carbon bond in above esters under the action of ethoxy anion is undoubtedly connected with strong inductive electron-withdrawing character of barene nucleus(3,4). The above fission of carbon-carbon bond can most likely be explained through the formation of barenyl anion as followed:

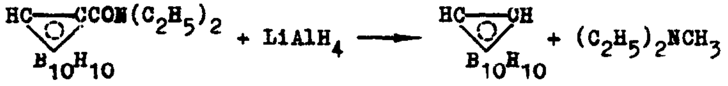


The data obtained on the easy cleavage of carbon-carbon bond in above esters under the action of ethoxy anion enable us to explain our earlier results on the hydrolysis of substituted barenecarboxylic acids. It was shown(3) that the hydrolysis of substituted barenecarboxylic acids with ethanolic KOH gives both the acids and the corresponding barenyl hydrocarbons:



From above results, it appeared that the formation of barenyl hydrocarbons proceeds through fission of carbon-carbon bond in initial esters. It should be noted that the hydrolysis of ethyl β-barenylpropionate (m.p.32°. Calcd.for $B_{10}C_7H_{20}O_2$: C, 34.42; H, 8.28; B, 44.26. Found: C, 34.81; H, 8.48; B, 44.34) with ethanolic KOH affords β-barenylpropionic acid (m.p. 147-149°. Calcd.for $B_{10}C_5H_{16}O_2$: C, 27.98; H, 7.40; B, 50.00. Found: C, 27.97; H, 7.19; B, 48.95) only.

Another example of cleavage of carbon-carbon bond have been found during the investigation of the interaction of lithium aluminium hydride with diethylamide of barenecarboxylic acid (m.p.109°. Calcd.for $B_{10}C_7H_{21}NO$: N, 5.76.Found: N, 5.94). It proved that in ether or tetrahydrofuran solution lithium aluminium hydride does not reduce the above amide to the corresponding amine but causes the fission of carbon-carbon bond between barene nucleus and amide group affording barene and methyldiethyl amine:



This reaction seems also to pass through the intermediate formation of barenyl anion.In contrast to diethylamide of barenecarboxylic acid, diethylamide of barenylacetic acid (m.p.82-83°. Calcd.for $B_{10}C_8H_{23}NO$: N, 5.45.Found: N, 5.40) is reduced by lithium aluminium hydride to β-barenylethyldiethyl amine (m.p.46.5-48°. Calcd.for $B_{10}C_8H_{25}N$: n, 5.78. Found: N, 5,76).The easy cleavage of carbon-carbon bond in above derivatives of barene under the action of bases confirms convincingly the thesis expressed formerly in our works that barene nucleus exhibits a strong inductive electron-withdrawing effect.

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