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THE METALATION OF BARENE AND ITS DERIVATIVES WITH THE AMIDES OF LITHIUM, SODIUM, POTASSIUM AND CALCIUM IN LIQUID AMMONIA

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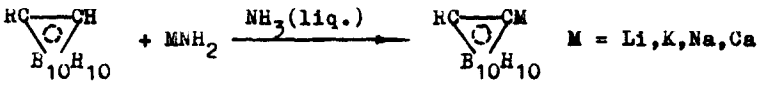
It was shown in the previous paper[1] that barene $B_{10}H_{10}C_2H_2$ and monosubstituted barenes[a] $B_{10}H_{10}C_2HR$ are metalated with sodium amide in boiling toluene with the formation of carbon-sodium derivatives. We have now found that the metalation of these organoboranes proceeds easily with the amides of lithium, sodium, potassium and calcium in liquid ammonia at low temperature and under atmospheric pressure like the metalation of α-acetylenes:



Barene gives both mono- and dimetallic derivatives. The alkali metal derivatives of barenes exhibit in liquid ammonia

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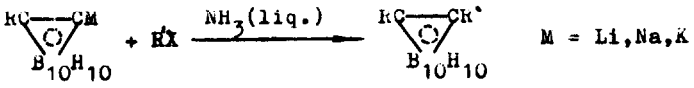
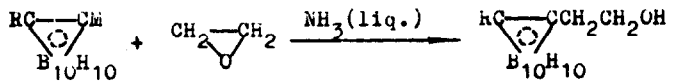
[a] American chemists use for these organoboranes the trivial name "carboranes"[2].

solution high reactivity and resemble the corresponding alkali metal derivatives of acetylenes, however the former are, it seems, more reactivity than the latter.The metal derivatives of barenes can be used in liquid ammonia solution for the preparation of various barenic compounds.

An important synthetic use of alkali metal derivatives of barenes in liquid ammonia is ready metathesis with alkyl and alkenyl halides (bromides and iodides) or with sulphates and p-toluenesulphonates to produce substituted barenes:

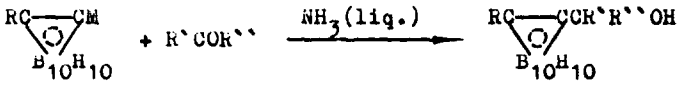


Thus, it was prepared from bromomethylbarene and methyl iodide (with $LiNH_2$ and $NaNH_2$) 1-bromomethyl-2-methylbarene[3]; m.p.123-124°; from phenylbarene and 1-bromo-3-chloropropane (with KNH_2) 1-(phenylbarenyl)-3-chloropropane, m.p.88-89° (Found: C, 45.01; H, 7.10; B, 36.45. $C_{11}H_{21}B_{10}Cl$ requires: C, 44.51; H, 7.08; B, 36.42)and from barene[4] and allyl bromide (with $LiNH_2$) allylbarene[5], m.p.61-62°. The alkali metal barenes gives in liquid ammonia with ethylene oxide the corresponding alcohols:

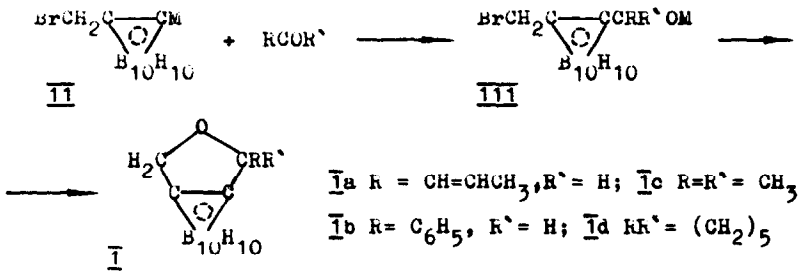


Thus, it was prepared from phenylbarene (with $LiNH_2$) β-(phenylbarenyl)ethanol, m.p.82-84°(Found: C, 44.47; H, 7.52; B, 40.89. $C_{10}H_{20}B_{10}O$ requires: C, 44.47; H, 7.58;

B, 40.98) and from barene (with $NaNH_2$) 1,2-bis-(β-hydroxyethyl)barene[5], m.p.124-125°. Another synthetic use of the metal derivatives of barenes in liquid ammonia solution involves their addition to the carbon-oxygen double bond of carbonyl compounds with the formation of the corresponding barenic carbinols:



We used this reaction for the synthesis of cyclic ethers (I) from metal derivatives of bromomethylbarene (II) and carbonyl compounds:



I a R = CH=CHCH$_3$, R' = H; I c R=R' = CH$_3$
I b R= C$_6$H$_5$, R' = H; I d RR' = (CH$_2$)$_5$

I are formed by cyclization of intermediate alcoholates (III). It was prepared from II and crotonic aldehyde (with $Ca/NH_2/_2$) Ia, m.p.71-72°(Found: C, 37.01; H, 8.08; B, 47.60. $C_7H_{18}B_{10}O$ requires: C, 37.18; H, 7.79; B, 47.807; from I and benzaldehyde (with $LiNH_2$) Ib, m.p.92-93°(Found: C, 45.85; H, 6.90; B, 41.13. $C_{10}H_{18}B_{10}O$ requires: C,45.85; H, 6.87; B,40.80); from II and acetone (with $NaNH_2$) Ic, m.p.61-62°

(Found: C, 33.93; H, 8.69; B, 50.59. $C_6H_{18}B_{10}O$ requires: C, 33.63; H, 8.42; B, 50.50) and from 11 and cyclohexanone (with KNH_2) 1d, m.p.76-77°(Found: C, 42.65; H, 8.71; B, 42.58. $C_9H_{22}B_{10}O$ requires: C, 42.55; H,8.66; B, 42.55).

It shoud be noted that after the preparation of the metal derivatives of barenes in liquid ammonia the latter can be replaced by another solvent.

The above examples show that the use of the alkali metal derivatives of barenes in liquid ammonia solution opens interesting possibilitys for the synthesis of various barenic compounds.

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