The metalation of 1-butyne and 1,2-butadiene with excess butyllithium

While making a survey of the reactivities of isomers of 1,2-butadiene with butyllithium in hexane solution, the following observations were made. One mole of 1-butyne reacted at once and completely with butyllithium to yield insoluble butynyllithium. The butynyllithium redissolved when another mole of butyllithium was added. One mole of 2-butyne showed no apparent sign of reaction with one mole of butyllithium except for a very slow deepening of color. One mole of 1,2-butadiene reacted slowly with one mole of butyllithium to yield a readily oxidizable, yellow solid which was insoluble in hexane. Hydrolysis of this solid yielded considerable 1-butyne. The above findings prompted a quantitative study of the reactions between 1-butyne as well as 1,2-butadiene with excess butyllithium.

Experimental

Reaction of 1-butyne with two moles of butyllithium to yield 3-methylpropynylenedilithium. A mixture consisting of 128.4 g of dry, olefin-free hexane and 2.8736 g of 97.88 % 1-butyne (0.0520 mole) was treated with 0.1040 mole of butyllithium as a 15 % solution in hexane, then the whole was sealed under lamp-grade nitrogen. A clear, yellow solution resulted at first, but in a few hours yellow crystals started to deposit. In the course of 210 h, yellow crystals separated leaving a colorless, supernatant liquid practically devoid of lithium. Titration of an aliquot of this well-mixed slurry (261 ml) indicated that 0.101 equivalent of alkali was present. A Gilman-Cartledge double titration[1] showed that 51.3 % of the lithium present in the slurry reacted with allyl bromide (under the conditions of the titration butynyllithium does not react with allyl bromide). A Ross-Trumbull double titration[2] showed that 96 % of the 1-butyne charged to the reaction mixture could be detected. Evaporation of an aliquot of the slurry to dryness in absence of air yielded a pyrophoric, yellow solid, 33.3 g of which contained one g-atom of lithium. Carbonation of a portion of slurry followed by hydrogenation resulted in a 39 % yield of 2-methylglutaric acid (m.p. 78°). The above results indicate that one mole of 1-butyne reacts with two moles of butyllithium to yield one mole of 3-methylpropynylenedilithium, $LiC{\equiv}C{-}CHLi{-}CH_3$.

A mixture of 0.03327 mole of 1-butyne and 0.06654 mole of butyllithium was made up in 71 ml of dry, olefin-free hexane in absence of air, then the clear yellow solution was carbonated at once. After the whole was hydrogenated 0.0341 mole of valeric acid and 0.0064 mole of 2-methylglutaric acid were obtained. During the 5-minute interval between mixing and carbonation 19 % of the butynyllithium had been converted into 3-methylpropynylenedilithium.

Reaction of 1,2-butadiene with two moles of butyllithium. A mixture of 101 g of dry, olefin-free hexane and 2.4430 g of 99.26 % 1,2-butadiene (0.04483 mole) was treated with 0.08966 mole of butyllithium as a 15 % solution in hexane, then the whole was sealed under lamp-grade nitrogen. After a reaction period of 256 h precipitation of gelatinous orange-yellow solid appeared to be complete. The colorless, supernatant liquid was practically devoid of lithium. Titration of an aliquot of the 208.5 ml of well-mixed slurry showed that 0.0808 equivalent of alkali was present. A Gilman-Cartledge double titration[1] showed that 60.8 % of the lithium in the slurry reacted with allyl bromide. A Ross-Trumbull double titration[2] showed that 77.8 % of the 1,2-butadiene charged to the reaction mixture could be detected as isomeric 1-butyne.

Evaporation of an aliquot of slurry to dryness in absence of air showed that 35.3 g of readily oxidizable, orange solid contained one g-atom of lithium. Carbonation of an aliquot of slurry followed by hydrogenation resulted in a 39 % yield of 2-methylglutaric acid (m.p. 79°). The above results show that one mole of 1,2-butadiene reacts incompletely with two moles of butyllithium to yield an insoluble solid whose composition corresponds to an association of one mole of 3-methylpropynylenedilithium with less than one mole of butyllithium.

Reaction of 1-butyne with three moles of butyllithium to form 3-methylpropynylenedilithium–butyllithium adduct. A mixture of 77.2 g of dry, olefin-free hexane and 2.7627 g of 97.88 % 1-butyne (0.0500 mole) was treated with 0.1500 mole of butyllithium as a 15 % hexane solution, then the whole was sealed under lamp-grade nitrogen. In the course of 1438 h precipitation of an orange, gelatinous solid appeared to be complete, as the nearly colorless supernatant liquid contained very little lithium. Titration of an aliquot of the 216 ml of well-mixed slurry showed that 0.146 equivalent of alkali was present. A Gilman-Cartledge double titration[1] showed that 74.5 % of the lithium present reacted with allyl bromide. A Ross-Trumbull double titration[2] of an aliquot of the slurry resulted in detection of 90.0 % of the charged 1-butyne. Evaporation of an aliquot of the slurry to dryness in absence of air showed that 39.9 g of orange-red, nearly pyrophoric solid contained one g-atom of lithium. Hydrolysis of an analytically weighed sample of the dry solid yielded the theoretical volume of C_4 gas (NTP), 52 % of which was 1-butyne and 48 % of which was butane. The above results indicated that one mole of 1-butyne reacts with three moles of butyllithium to yield 3-methylpropynylenedilithium–butyllithium adduct.

Reaction of 1-butyne with four moles of butyllithium. A mixture of 0.050 mole of 1-butyne and 100 g of dry, olefin-free hexane was treated with 0.200 mole of butyllithium as a 15 % solution in hexane, then the whole was sealed under lamp-grade nitrogen. In the course of 133 days, only a trace of yellow precipitate came down.

Reaction of 1,2-butadiene with three and four moles of butyllithium. Two identical solutions consisting of 0.050 mole of 1,2-butadiene in 100 g of dry, olefin-free hexane were prepared. Fifteen percent butyllithium solution in hexane to the extent of 0.150 mole and 0.200 mole, respectively, was added to the above mixtures, then each was sealed under lamp-grade nitrogen. In the course of 119 days, only a trace of yellow precipitate came down from each reaction mixture.

Discussion and conclusions

Two moles of butyllithium react with one mole of 1-butyne to yield hexane-insoluble 3-methylpropynylenedilithium[3]. Half of the lithium in this compound should react quickly with ethereal allyl bromide, and 32.98 g should contain one g-atom of lithium. Carbonation of 3-methylpropynylenedilithium followed by hydrogenation will yield 2-methylglutaric acid.

$$HC{\equiv}C{-}CH_2{-}CH_3 + C_4H_9Li \longrightarrow LiC{\equiv}C{-}CH_2{-}CH_3 + C_4H_{10}$$

$$LiC{\equiv}C{-}CH_2{-}CH_3 + C_4H_9Li \longrightarrow LiC{\equiv}C{-}CHLi{-}CH_3 + C_4H_{10}$$

Three moles of butyllithium react with one mole of 1-butyne to yield a hexane-insoluble adduct of 3-methylpropynylenedilithium and butyllithium. Two-thirds of the lithium in this compound should react quickly with ethereal allyl bromide, and

43.33 g should contain one g-atom of lithium. Hydrolysis of such an adduct will yield an equivolume mixture of 1-butyne and butane.

$$\mathrm{LiC{\equiv}C{-}CHLi{-}CH_3 + C_4H_9Li \longrightarrow LiC{\equiv}C{-}CHLi{-}CH_3{\cdot}C_4H_9Li}$$

One mole of 1,2-butadiene reacts incompletely with two moles of butyllithium to yield a hexane-insoluble mixture consisting of one mole of 3-methylpropynylenedilithium associated with less than one mole of butyllithium.

$$(1-x)\mathrm{CH_2{=}C{=}CH{-}CH_3} + 2\mathrm{C_4H_9Li} \rightarrow (1-x)\mathrm{LiC{\equiv}C{-}CHLi{-}CH_3}\cdot 2x\mathrm{C_4H_9Li} + (2-2x)\mathrm{C_4H_{10}}$$
where $x < 1/4$

Alkyllithium compounds have been found to occur as associated species in hydrocarbon solution. The solubility of ethyllithium in benzene is enhanced by the addition of *tert*-butyllithium[4]. Experiment shows that one mole of hexane-insoluble butynyllithium readily dissolves in a hexane solution containing one mole of butyllithium. However, the butyllithium at once starts to metalate the butynyllithium to form 3-methylpropynylenedilithium which remains in solution until the concentration of butyllithium falls to a low figure. 3-Methylpropynylenedilithium is so insoluble in hexane that it can form an insoluble 1:1 adduct with butyllithium. Apparently the association of one mole of 3-methylpropynylenedilithium with two moles of butyllithium results in a soluble adduct for the reaction mixture of one mole of 1-butyne with four moles of butyllithium in hexane yields no insoluble phase.

At this writing there is no evidence to show that 3-methylpropynylenedilithium can be further metalated with butyllithium to yield a trilithium-substituted 1-butyne. A trilithium-substituted 1-butyne should be expected to be very insoluble in hexane.

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