Organometallic Compounds of the Alkali Metals. Part V.* The Non-radical Decomposition of n-Butyl-lithium.

By D. Bryce-Smith.

Solutions of *n*-butyl-lithium in *iso*propylbenzene decompose at 135° with the evolution of butane and butene, the latter slightly predominating : 2 : 3-dimethyl-2 : 3-diphenylbutane is not formed. In contrast, photolysis both of di-*n*-butylmercury and of a mixture of *n*-butyl iodide and silver in *iso*propylbenzene leads to evolution of butane and a little butene : 2 : 3-dimethyl-2 : 3-diphenylbutane is produced in each case. From this evidence, and from earlier work, it is concluded that thermal decomposition of alkali-metal alkyls does not produce alkyl radicals.

MORTON AND CLUFF (*J. Amer. Chem. Soc.*, 1952, **74**, 4056; 1953, **75**, 134) reported the isolation of metallic sodium on thermal decomposition of *n*-pentylsodium, and concluded that radicals are present under those conditions where *n*-pentylsodium is used : $n\text{-}C_5H_{11}Na \longrightarrow n\text{-}C_5H_{11} \cdot + Na$ (of. Morton and Newey, *ibid.*, 1942, **64**, 2247). Such behaviour, while recalling that of, *e.g.*, alkyl-mercury and -lead compounds, is difficult to reconcile with various other observations. Thus, Carothers and Coffman (*ibid.*, 1929, **51**, 588) found that thermal decomposition of ethylsodium was best represented by the equation, $C_2H_5Na \longrightarrow C_2H_4 + NaH$. Sodium was produced at temperatures above 142° by dissociation of sodium hydride. Ziegler and Gellert (*Annalen*, 1950, **567**, 179) obtained broadly similar results for the thermal decomposition of ethyl- and *n*-butyl-lithium. It is, of course, well known that the thermal-decomposition stage of Tschitschibabin-type reactions involves the elimination of alkali-metal hydride. In Part III (*J.*, 1954, 1079), no evidence was found for the formation of *n*-pentyl radicals when *n*-pentylsodium was suspended in *iso*propylbenzene under conditions where appreciable thermal decomposition of the reagent must have occurred. Free *n*-pentyl radicals would have been expected to produce αα-dimethylbenzyl radicals by abstraction of hydrogen from the medium, and the latter radicals should then have dimerised to 2 : 3-dimethyl-2 : 3-diphenylbutane. No trace of the dimer was obtained from this or from similar reactions when alkylpotassium compounds were used.†

In the present work, *iso*propylbenzene was used as a detector for possible free-radical intermediates in the thermal decomposition of *n*-butyl-lithium. This comparatively non-polar lithium compound seemed to offer a better chance of homolytic dissociation than would the more polar sodium or potassium compounds. This decomposition at 135° gives no 2 : 3-dimethyl-2 : 3-diphenylbutane. In addition to the butene expected from the reaction, $n\text{-}C_4H_9Li \longrightarrow n\text{-}C_4H_8 + LiH$, some butane is evolved. Formation of the saturated hydrocarbon in smaller amount was observed by Ziegler and Gellert (*loc. cit.*; cf. Carothers and Coffman, *loc. cit.*) both in " dry " decompositions and in the presence of *n*-octane. They very reasonably ascribed it to metallation of the olefin : $CH_3 \cdot CH_2 \cdot CH = CH_2 + n\text{-}C_4H_9Li \longrightarrow CH_3 \cdot CHLi \cdot CH = CH_2 + n\text{-}C_4H_{10}$. In the present case, some metallation of the solvent also occurred. The formation of butane does not imply the intermediate production of butyl radicals.

To confirm the belief that the non-formation of 2 : 3-dimethyl-2 : 3-diphenylbutane was truly diagnostic of a non-radical reaction, *n*-butyl radicals were generated in *iso*propylbenzene by two methods, (*a*) photolysis of di-*n*-butylmercury and (*b*) photolysis of a mixture of *n*-butyl iodide and silver powder. [These reactions were chosen in the belief that only one radical species would be formed : the two C–Hg bonds in dialkylmercury compounds

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are believed to break simultaneously (Chilton and Gowenlock, *Trans. Faraday Soc.*, 1953, **49**, 1451; 1954, **50**, 824)]. 2 : 3-Dimethyl-2 : 3-diphenylbutane was obtained in each case, and the gas evolved was 85—90% butane with 10—15% of butene. Decomposition of *n*-butyl iodide was very incomplete and the yield of 2 : 3-dimethyl-2 : 3-diphenylbutane was low : the yield from di-*n*-butylmercury was nearly 50%. The virtual non-formation of *n*-octane indicates that the stationary concentration of *n*-butyl radicals was much lower than that of αα-dimethylbenzyl radicals, as one would expect from their relative reactivities. Little or no fragmentation of *n*-butyl radicals was detected. Although new in their present application, these photodecompositions provide unquestionable sources of *n*-butyl radicals, and they can be extended to the production of phenyl radicals in solution (Bryce-Smith, Hey, and Pengilly, unpublished work). They confirm the view that *n*-butyl radicals are not formed during the thermal decomposition of *n*-butyl-lithium. From the results quoted in Part III (*loc. cit.*) and discussed above, a similar conclusion applies to the decomposition of alkyl-sodium and -potassium compounds. Morton and Cluff's results (*locc. cit*) are hard to understand; but their significance is put in some doubt by the apparent failure to ascertain what excess of sodium remained from the initial preparation of *n*-pentylsodium.

EXPERIMENTAL

Thermal Decomposition of n-*Butyl-lithium in* iso*Propylbenzene.*—A 1·71N-solution of *n*-butyl-lithium in *n*-pentane was prepared as described in Part II (*J.*, 1953, 861). *n*-Pentane was distilled under reduced pressure from 25 ml. (0·043 mole) of the clear solution and 50 ml. of dried (CaH$_2$), freshly refractionated *iso*propylbenzene were then added. At 135° (nitrogen atmosphere), a pale brown solid was precipitated (presumably lithium hydride) and gas was steadily evolved. After 24 hr. at 135°, the dark brown product was cooled and poured on solid carbon dioxide and ether. Addition of water produced a brisk evolution of hydrogen, but the brown colour was not discharged. Washing of the separated organic layer with water removed most of the coloured material. The combined aqueous layers were acidified and extracted with light petroleum (b. p. <40°). Removal of the solvent gave 0·02 g. of an oily colourless mixture of cuminic acids. The amount was too small for analysis by the method described in Part III (*loc. cit.*), but from the rapid reduction of warm alkaline permanganate it is likely that nuclear isomers predominated. Fractional distillation of the dried *iso*propylbenzene solution gave no octane (judged by refractive indices). The material of b. p. >180° amounted to 0·3 g. Chromatography on alumina gave 0·05 g. of an oil with an odour resembling that of the higher alkylbenzenes, but no trace of 2 : 3-dimethyl-2 : 3-diphenylbutane or other crystalline material.

The gas evolved during the thermal decomposition was found to contain *ca.* 60% of butene and 40% of butane. No lower-boiling hydrocarbons were detected.

Photolysis of Di-n-*butylmercury in* iso*Propylbenzene.*—A solution of di-*n*-butylmercury (6·05 g., 0·0192 mole) in dry *iso*propylbenzene (25 ml.) was irradiated with ultraviolet light under nitrogen in a quartz flask for 25 hr. at 135°. A 200-w medium-pressure mercury-vapour lamp was used at a distance of 1 cm. from the vessel : it also served as a heater, and the flask temperature was regulated by means of a current of cold air. Mercury (3·5 g., 91%) was removed by filtration. Fractional distillation and refractive-index measurements showed the presence of not more than 0·05 g. (2%) of octane. The pale yellow residue, b. p. >160°, was treated with methyl alcohol to give 1·95 g. (43% based on di-*n*-butylmercury; 47% based on mercury liberated) of 2 : 3-dimethyl-2 : 3-diphenylbutane, m. p. 117°. One recrystallisation from ethyl alcohol gave pure material, m. p. and mixed m. p. 118·5°.

The gas evolved during the photolysis was found to be a mixture of butane 85% and butene 15%, with no more than traces of lower-boiling hydrocarbons.

In a control experiment, irradiation of *iso*propylbenzene under nitrogen in the presence of mercury gave no detectable amount of 2 : 3-dimethyl-2 : 3-diphenylbutane.

Photolysis of n-*Butyl Iodide in* iso*Propylbenzene.*—Preliminary experiments showed that although iodine is rapidly liberated by the irradiation of solutions of *n*-butyl iodide in *iso*propylbenzene, decomposition soon becomes very slow, presumably owing to absorption of the radiation by iodine. Silver powder was added in order to overcome this difficulty. It reacts with iodine but is inert to *n*-butyl iodide.

A solution of *n*-butyl iodide (3·7 g., 0·02 mole) in dry *iso*propylbenzene (20 ml.) was stirred with silver powder (3·25 g., 0·03 g.-atom) and irradiated as above at 125—135° for 35 hr. under

nitrogen. Most of the *n*-butyl iodide was recovered, but 0·15 g. of 2 : 3-dimethyl-2 : 3-diphenyl-butane, m. p. 116° and mixed m. p. 116·5°, was obtained. The small amount of gas which was evolved was found to be a mixture of butane *ca.* 90% and butene 10%.

This work has been carried out during the tenure of an I.C.I. Research Fellowship at the University of London.