

318. *Organometallic Compounds of the Alkali Metals. Part VI.*
Evidence for the Formation of Free Alkyl Radicals during Certain
Wurtz Reactions. Homolytic Reactions between Alkyl-lithium Com-
pounds and Alkyl Halides.†*

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*iso*Propylbenzene has been used to detect the formation of free alkyl radicals during certain reactions of the Wurtz type. With *n*-butyl iodide at 130°, the tendency to form free *n*-butyl radicals decreases in the order lithium > sodium > potassium. The free radicals are largely, if not entirely, produced by a reaction of the type, $RM + RHal \longrightarrow 2R\cdot + MHal$, rather than $RHal + M \longrightarrow R\cdot + MHal$. The evidence indicates that free radicals play only a minor part in the formation of the usual Wurtz coupling and disproportionation products.

n-Butyl-lithium with iodine gives *n*-butyl iodide, which may then react with excess of *n*-butyl-lithium to give *n*-butyl radicals.

n-Butyl radicals, from *n*-butyl bromide and *n*-butyl-lithium, are relatively unreactive towards benzene, giving a trace of *n*-butylbenzene but no diphenyl.

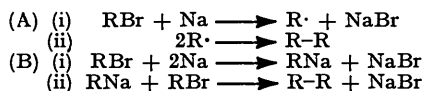
ALTHOUGH it is well known from the work of Polanyi and his co-workers (reviewed by Warhurst¹) that alkyl halides with sodium vapour at elevated temperatures and low pressures produce free alkyl radicals, it has for long been uncertain whether a comparable reaction occurs in solution at lower temperatures under the usual conditions of the Wurtz

* Part V, *J.*, 1955, 1712.

† An account of some of the present results was presented at the Symposium on Organometallic Compounds, Manchester, in April, 1955: see *Nature*, 1955, **176**, 60.

¹ Warhurst, *Quart. Rev.*, 1951, **5**, 44.

reaction. Two basically different mechanisms have been proposed and supported by various workers :



The free-radical mechanism (A) was first suggested by Schlubach and Goes² but, although its possibility has received much subsequent discussion, there seems to be little definite experimental support. The "sodium flame" reactions¹ and the Ullmann reaction³ both involve free radicals, and rather unsafe analogies have sometimes been noted between these and the Wurtz reaction. Bachmann and Clarke⁴ isolated *o*-terphenyl and triphenylene from the reaction between chlorobenzene and sodium at 130° and regarded the production of these compounds as evidence for the intermediate formation of free phenyl radicals; but Dewar⁵ and Morton, Davidson, and Hakan⁶ have suggested alternative non-radical explanations. In the light of recent work,⁷ it seems that the reaction of chlorobenzene with phenylsodium might well lead to the formation of "benzyne," C₆H₄, the trimerisation of which to triphenylene has been reported by Luttringhaus and Schubert.⁷ Kharasch, Holton, and Nudenberg⁸ treated *sec.*- and *tert.*-butyl bromide with sodium in the presence of isoprene. They obtained products which suggested an interaction between the free alkyl radicals and isoprene, but appeared not to regard their results as wholly conclusive.

Mechanism (B) seems to be more widely supported. The formation of alkali-metal alkyls during Wurtz-type reactions has been demonstrated on many occasions, and by suitable choice of conditions, alkyls of lithium,⁹ sodium,¹⁰ and potassium¹¹ have been prepared. Morton and his co-workers⁶ concluded from an extensive investigation that all the coupling and disproportionation products of Wurtz reactions could be accounted for without an assumption of free-radical intermediates, although they did not wholly exclude the possibility that free radicals play a small part (cf. Morton and Brachman;¹² Morton and Cluff¹³). Many workers¹⁴ have studied the coupling and disproportionation reactions which occur between alkali-metal alkyls and alkyl halides. The results, which are complex, appear not to have suggested the possibility of free-radical intermediates.

In the present work, *isopropylbenzene* has been used as a detector for possible free-radical intermediates in the Wurtz reaction and in some related reactions. In earlier Parts of this series^{15, 16} it was shown that *isopropylbenzene* does not produce free alkyl radicals during its reactions with alkali-metal alkyls, and the difficulties inherent in the use of isoprene as a radical detector are therefore avoided.

EXPERIMENTAL

*iso*Propylbenzene was purified by shaking B.D.H. material with portions of concentrated sulphuric acid until the acid remained almost colourless, washing, drying, and then distilling it over calcium hydride and sodium through a 180-cm. column of Fenske helices. A middle fraction boiling over 0.3° was used. The hydrocarbon was stored over a little powdered calcium hydride to keep it dry and to prevent the formation of peroxide. (We have found sodium

² Schlubach and Goes, *Ber.*, 1922, **55**, 2889.

³ (a) Rapson and Shuttleworth, *Nature*, 1941, **147**, 675; (b) Nursten, *J.*, 1955, 3081.

⁴ Bachmann and Clarke, *J. Amer. Chem. Soc.*, 1927, **49**, 2089.

⁵ Dewar, "Electronic Theory of Organic Chemistry," Oxford, 1949, pp. 258—259.

⁶ Morton, Davidson, and Hakan, *J. Amer. Chem. Soc.*, 1942, **64**, 2242.

⁷ Luttringhaus and Schubert, *Naturwiss.*, 1955, **42**, 17; Roberts *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 3290.

⁸ Kharasch, Holton, and Nudenberg, *J. Org. Chem.*, 1955, **20**, 920.

⁹ Ziegler and Colonius, *Annalen*, 1930, **479**, 135.

¹⁰ Morton and Hechenbleikner, *J. Amer. Chem. Soc.*, 1936, **58**, 1697.

¹¹ Morton, Brown, Holden, Letsinger, and Magat, *ibid.*, 1945, **67**, 2224.

¹² Morton and Brachman, *ibid.*, 1954, **76**, 2973, 2980.

¹³ Morton and Cluff, *ibid.*, 1952, **74**, 4056; 1953, **75**, 134.

¹⁴ (a) Morton and Richardson, *ibid.*, 1940, **62**, 123; (b) Whitmore and Zook, *ibid.*, 1942, **64**, 1783;

(c) Ulrich *et al.*, *ibid.*, 1950, **72**, 5127, 5130, 5132; (d) Letsinger and Traynham, *ibid.*, p. 849; (d) Cristol *et al.*, *ibid.*, 1951, **73**, 810, 813. [Further references are there cited.]

¹⁵ Bryce-Smith, *J.*, 1955, 1712.

¹⁶ Bryce-Smith, *J.*, 1954, 1079.

hydride and calcium hydride to be very useful in this respect for a number of hydrocarbons and ethers.) Alkyl halides were purified as in Part I.¹⁷ Alkyl iodides contained no free iodine. Solutions of alkyl-lithium compounds in aromatic solvents were prepared as in Part II: ¹⁸ free metal and lithium halides were excluded.

Alkali metals were used in the form of wire (0.5 mm. diam.), except where otherwise stated. All reactions were carried out under nitrogen, with stirring.

It was not found practicable to separate *n*-octane (b. p. 126°) from *isopropylbenzene* (b. p. 151°) by fractional distillation. A composition–refractive index curve was constructed from which the proportions of *n*-octane in the experimental mixtures with *isopropylbenzene* were found.

The yields of 2 : 3-dimethyl-2 : 3-diphenylbutane refer to material of m. p. >114°. The pure compound, m. p. 118–118.5°, was obtained by recrystallisation from ethyl alcohol or, in difficult cases, by passing a solution in light petroleum through a column of alumina. Mixed m. p.s were always taken.

Reactions between Alkali Metals and Alkyl Iodides.—(a) *Sodium and ethyl iodide.* A dispersion of sodium (2.0 g., 0.087 g.-atom) in *isopropylbenzene* (35 g.) was stirred with ethyl iodide (15.6 g., 0.1 mole) at 90–95° for 20 hr. The product was filtered through sintered glass under nitrogen. The material (*ca.* 0.3 g.), b. p. >160°, partly crystallised after 10 days. Addition of a little 1 : 1 methanol–ethanol gave 2 : 3-dimethyl-2 : 3-diphenylbutane (0.03 g., 0.3%).

(b) *Lithium and n-butyl iodide.* (i) At 95°. *n*-Butyl iodide (9.2 g., 0.05 mole) was heated with lithium (1.05 g., 0.15 g.-atom) in *isopropylbenzene* (24 g.) for 18 hr. The product was filtered as in method (a). The yields of 2 : 3-dimethyl-2 : 3-diphenylbutane and *n*-octane were 1.1 g. (19%) and 1.0 g. (35%) respectively.

(ii) At 130°. The previous experiment was repeated at 130° with *n*-butyl iodide (11.0 g., 0.06 mole) and lithium (1.25 g., 0.18 g.-atom) in *isopropylbenzene* (29 g.). Butane (20%) and butene (10%) were collected in a trap at –25°. Traces of lower-boiling hydrocarbons appeared to be also formed, suggesting slight fragmentation of butyl radicals. Titration of an aliquot ¹⁸ showed that 0.003 mole (5%) of a soluble organometallic species was formed, possibly *n*-butyllithium. After hydrolysis, the yields of 2 : 3-dimethyl-2 : 3-diphenylbutane and *n*-octane were 1.2 g. (18%) and 0.8 g. (24%) respectively.

(c) *Sodium and n-butyl iodide.* (i) at 25°. *n*-Butyl iodide (9.2 g., 0.05 mole) was added during 1 hr. to sodium (3.5 g., 0.152 g.-atom) in *isopropylbenzene* (24 g.). The blue product was kept at *ca.* 20° for 2 days. A small portion gave a negative test for butylsodium.¹⁹ Butane (1.6%) and butene (1.4%) were pumped off. After hydrolysis, *n*-octane (2.35 g., 83%) was obtained, but no trace of 2 : 3-dimethyl-2 : 3-diphenylbutane could be detected.

(ii) The previous experiment was repeated on a larger scale, and with an excess of *n*-butyl iodide. *n*-Butyl iodide (22.0 g., 0.12 mole), sodium (2.3 g., 0.1 g.-atom), and *isopropylbenzene* (48 g.) gave butane (5.7%), butene (5.3%), and *n*-octane (4.7 g., 69%); but again, no 2 : 3-dimethyl-2 : 3-diphenylbutane was found. The estimation of *n*-octane was complicated by the necessity to remove the excess of *n*-butyl iodide (b. p. 130°) by heating the *isopropylbenzene*-*n*-octane mixture with alcoholic potassium hydroxide. The figure quoted may be rather low.

(iii) At 130°. *n*-Butyl iodide (13.8 g., 0.075 mole) was added during 30 min. to sodium (5.2 g., 0.225 g.-atom) in *isopropylbenzene* (36 g.). After a further 15 min., the grey product was briefly heated at 150° in order to expel all butane and butene. Butane (0.46 g., 10.5%), butene (0.15 g., 3.5%), *n*-octane (2.6 g., 61%), and 2 : 3-dimethyl-2 : 3-diphenylbutane (0.11 g., 1.2%) were obtained.

(iv) Experiment (c) (ii) was repeated, but, before addition of water, the blue reaction product was heated for 1 hr. at 130°, at which temperature all colour was rapidly discharged. No 2 : 3-dimethyl-2 : 3-diphenylbutane was obtained.

(d) *Potassium and n-butyl iodide at 130°.* *n*-Butyl iodide (22.0 g., 0.12 mole) was added during 30 min. to potassium (3.9 g., 0.1 g.-atom) in *isopropylbenzene* (48 g.). *n*-Octane (2.0 g., 29%) was formed. Distillation at 20 mm. gave fractions, b. p. (i) 120–130° (1.0 g.) and (ii) 130–160° (0.5 g.), together with an oily residue (0.5 g.). Fraction (i) was probably largely *n*-butyl-*isopropylbenzenes* (Found: C, 88.1; H, 11.35. Calc. for C₁₃H₂₀: C, 88.6; H, 11.4%). Treatment with ethanol gave, after prolonged storage, 2 : 3-dimethyl-2 : 3-diphenylbutane (2 mg., 0.02%). This was not quite pure, having m. p. 111–113° and mixed m. p. 112–114°.

¹⁷ Bryce-Smith and Turner, *J.*, 1950, 1975.

¹⁸ Bryce-Smith and Turner, *J.*, 1953, 861.

¹⁹ Gilman and Schulz, *J. Amer. Chem. Soc.*, 1925, 47, 2002.

Reactions between Alkyl Halides and Alkali-metal Alkyls.—(e) *n*-Butyl chloride and *n*-butyl-lithium. A solution of *n*-butyl-lithium (0.043 mole) in isopropylbenzene (41 g.) was heated with *n*-butyl chloride (4.15 g., 0.045 mole) at 95° (inner temp.) for 6 days. There was an induction period of 1 hr. before the solution became turbid owing to precipitation of lithium chloride. Titration of an aliquot portion of the supernatant liquid showed that only a trace of *n*-butyl-lithium remained. After treatment with water, the separated and dried organic layer was fractionated. The fraction of b. p. 125—151° contained *n*-octane (1.4 g., 29%). The colourless material, b. p. >160° (1.66 g.), solidified on cooling. Recrystallisation from methanol gave pure 2 : 3-dimethyl-2 : 3-diphenylbutane (1.21 g., 12%).

(f) *n*-Butyl bromide and *n*-butyl-lithium. (i) At 20—25°. *n*-Butyl bromide (12 g., 0.088 mole), *n*-butyl-lithium (0.043 mole), and isopropylbenzene (16 g.) gave, after five days, *n*-octane (2.5 g., 51%) and 2 : 3-dimethyl-2 : 3-diphenylbutane (1 g., 9%). The induction period was 2 hr.

(ii) At 60°. *n*-Butyl bromide (5.8 g., 0.0425 mole), *n*-butyl-lithium (0.0405 mole), and isopropylbenzene (39 g.) gave, after 3 days, *n*-octane (1.8 g., 40%) and 2 : 3-dimethyl-2 : 3-diphenylbutane (1.6 g., 17%). The induction period was 5 min.

(iii) At 95°. *n*-Butyl bromide (5.35 g., 0.039 mole), *n*-butyl-lithium (0.0376 mole), and isopropylbenzene (36 g.) gave, after 18 hr., butane (19.5%), butene (3.5%), *n*-octane (2.1 g., 43%), 2 : 3-dimethyl-2 : 3-diphenylbutane (1.6 g., 18%), and lithium hydride (9%). This last was evidently derived from thermal decomposition of *n*-butyl-lithium.¹⁵ In addition, a colourless liquid, b. p. 220—255° (ca. 0.5 g.), was obtained, which may have been a mixture of *n*-butylisopropylbenzenes. The induction period was $\frac{1}{2}$ min.

(g) *n*-Butyl iodide and *n*-butyl-lithium. (i) At 95°. *n*-Butyl iodide (7.2 g., 0.039 mole) was added during 10 min. to *n*-butyl-lithium (0.0376 mole) in isopropylbenzene (36 g.). There was an instant precipitate of lithium iodide and the mildly exothermic reaction was 91% complete after 70 min. After addition of water, *n*-octane (1.45 g., 35%) and 2 : 3-dimethyl-2 : 3-diphenylbutane (1.15 g., 14%) were obtained, together with liquid fractions with the following b. p.s: (i) <245° (0.2 g.), (ii) 245—255° (1.9 g.), (iii) 255—280° (0.2 g.); and a pale yellow residue (0.3 g.): fractions (i)—(iii) were moderately unsaturated to bromine in carbon tetrachloride. Fraction (ii) would correspond to *n*-butylisopropylbenzenes, but the analysis indicated two fewer hydrogen atoms per molecule (Found: C, 89.75; H, 10.2. Calc. for C₁₃H₂₀: C, 88.6; H, 11.4. Calc. for C₁₃H₁₈: C, 89.6; H, 10.4%). Oxidation of the hydrocarbon (0.1931 g.) with chromium trioxide (2.1 g.) in acetic acid (3 ml.) at 130° for 24 hr. gave terephthalic acid (0.0116 g.) (dimethyl ester, m. p. and mixed m. p. 141°) and benzoic acid (0.0187 g.), m. p. 120° and mixed m. p. 120—121°. *iso*Phthalic acid was shown to be absent by the test with thallos acetate.²⁰

In a duplicate experiment, the yield of 2 : 3-dimethyl-2 : 3-diphenylbutane was 15%.

(ii) At 60°. *n*-Butyl iodide (7.8 g., 0.0425 mole), added during 30 min. to *n*-butyl-lithium (0.045 mole) in isopropylbenzene (39 g.), gave, after a further 2 $\frac{1}{2}$ hr. at 60°, 2 : 3-dimethyl-2 : 3-diphenylbutane (0.9 g., 9.5%). Other products were not investigated. The induction period was $\frac{1}{2}$ min.

(h) *sec*-Butyl bromide and *sec*-butyl-lithium at 95°. *sec*-Butyl bromide (5.6 g., 0.041 mole) was added during 30 min. to *sec*-butyl-lithium (0.039 mole) in isopropylbenzene (37.5 g.). There was an immediate exothermic reaction. Unexpectedly, the evolution of gas almost ceased after the addition of little more than half of the halide. After 5 hr. at 95°, the titres of hydrolysed 1-ml. portions of the supernatant liquid and the stirred suspension were 0.78 ml. and 1.40 ml. of 0.2*N*-hydrochloric acid respectively: after a further 18 hr. the corresponding titres were 0.47 and 1.35 ml. A test with Michler's ketone¹⁹ on a sample of the stirred suspension was negative: a control test with *sec*-butyl-lithium was strongly positive. These facts suggest that lithium hydride may have been formed. After the addition of water, 2 : 3-dimethyl-2 : 3-diphenylbutane (0.55 g., 6%) was obtained, together with ca. 1 g. of an unidentified liquid, b. p. 110—150°/8 mm.

(i) *n*-Butyl iodide and *n*-butylsodium at 25°. *n*-Butylsodium was prepared by the addition of di-*n*-butylmercury (10.0 g., 0.0318 mole) to sodium (1.47 g., 0.064 g.-atom) in *n*-pentane (30 ml.). After 24 hr., *n*-pentane was removed under reduced pressure, and the solid residue was kept under 0.05 mm. pressure for 5 min. before addition of isopropylbenzene (60 g.) and, during 1 hr., of *n*-butyl iodide (12.9 g., 0.07 mole). After 1 hr. more of stirring at 20—25°, butane (27%) and butene (10%) were pumped off. The reaction product was filtered under nitrogen without treatment with water. The material of b. p. >160° (0.2 g.) partly

²⁰ Bryce-Smith, *Chem. and Ind.*, 1953, 244.

crystallised on long storage. Recrystallisation gave 2 : 3-dimethyl-2 : 3-diphenylbutane (0.050 g., 0.4%).

(j) *Reaction of n-butyl-lithium with iodine.* Dry, finely powdered iodine (5.2 g., 0.0205 mole) was added in 30 min. from a gas-tight hopper to *n*-butyl-lithium (0.0405 mole) in isopropylbenzene (39 g.) at 60°. The colourless product was kept at this temperature for a further 18 hr. After filtration from lithium iodide, fractional distillation gave a fraction, b. p. 125—145°, which was shown to contain *n*-butyl iodide by the formation of *S*-*n*-butylthiuronium picrate (0.5 g.), m. p. and mixed m. p. 176—177°. Addition of methanol containing a little ethanol to the material of b. p. > 160° gave 2 : 3-dimethyl-2 : 3-diphenylbutane (0.5 g., 10%). Cf. experiment (g)(ii).

(k) *Reaction of n-butyl-lithium with n-butyl bromide in benzene.* *n*-Butyl bromide (5.35 g., 0.039 mole) was added in 30 min. to a refluxing solution of *n*-butyl-lithium (0.0376 mole) in benzene (40 ml.). The mixture was heated under reflux for a further 6 hr., cooled, and treated with water. Fractional distillation of the dried organic layer gave fractions with the following b. p.s.: (i) 110—175° (0.3 g.), (ii) 175—185° (0.1 g.), (iii) 185—240° (0.3 g.); and an oily residue (1 g.). Infrared spectra of (i)—(iii) closely resembled the spectrum of pure *n*-butylbenzene (kindly taken by Mr. R. J. D. Smith), except that the overall transmissions were greater. This suggested that *n*-butylbenzene was present in admixture with material relatively transparent over the range examined (4—15 μ). Control experiments showed that as little as 10% of diphenyl in the mixture would have been detected had it been present.

Butane (1.2 g., 28%) and butene (0.5 g., 12%) were evolved during the reaction.

To investigate the possibility that *n*-butylbenzene was produced by a direct reaction between *n*-butyl-lithium and benzene, a solution of *n*-butyl-lithium (0.085 mole) in benzene (50 ml.) was heated under reflux for 7 days. The gas evolved (2.3 g.) was a mixture of butane (16%) and butene (84%). No trace of *n*-butylbenzene was detected, and the main reaction was evidently a thermal decomposition which did not involve the solvent (cf. Part V¹⁵).

DISCUSSION

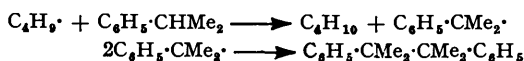
Some of the present results are summarised in the Table.

Yields (%) of products from the reactions of halides with alkali metals and alkali-metal alkyls.

Halide	Metal reagent	Temp.	"Dicumyl" *	Octane	Butane	Butene	Butane : butene
<i>n</i> -C ₄ H ₉ I	Li	95°	19	35			
"	"	130	17	24	20	10	2.0
"	Na	25	0.0	83	1.6	1.4	1.15
"	"	130	1.2	61	10.5	3.5	3.0
"	K	130	0.02	29			3.0
<i>n</i> -C ₄ H ₉ Cl	<i>n</i> -C ₄ H ₉ Li	95	12	29			
<i>n</i> -C ₄ H ₉ Br	"	95	18	43	19.5	3.5	5.6
<i>n</i> -C ₄ H ₉ I	"	95	14	35			
<i>n</i> -C ₄ H ₉ Br	"	25	9	50			
<i>n</i> -C ₄ H ₉ I	"	60	9.5				
<i>n</i> -C ₄ H ₉ Br	"	60	17	40			
<i>sec.</i> -C ₄ H ₉ Br	<i>sec.</i> -C ₄ H ₉ Li	95	6				1.5
<i>n</i> -C ₄ H ₉ I	<i>n</i> -C ₄ H ₉ Na	25	0.4		27	10	2.7
I ₂	<i>n</i> -C ₄ H ₉ Li	60	10				

* 2 : 3-Dimethyl-2 : 3-diphenylbutane. Blank spaces in the Table indicate that no measurement was made.

It is considered that the production of 2 : 3-dimethyl-2 : 3-diphenylbutane in these various reactions indicates that free butyl radicals are formed, and that they abstract hydrogen from the solvent as follows :



In Part V¹⁵ of this Series, *n*-butyl radicals which were generated by photolysis of (a) di-*n*-butylmercury and (b) a mixture of *n*-butyl iodide and silver were shown to react with isopropylbenzene in the above manner. Moreover, it has been shown that the decomposition of *n*-butyl-lithium¹⁵ and of sodium and potassium alkyls¹⁶ in isopropylbenzene produces no 2 : 3-dimethyl-2 : 3-diphenylbutane. Neither the alkali metals used

nor the alkyl halides react with *isopropylbenzene* under the conditions of the present experiments.

Particular attention may be drawn to the following points. (a) The yields of 2 : 3-dimethyl-2 : 3-diphenylbutane from the reactions between alkali metals and *n*-butyl iodide under corresponding conditions decreased in the order lithium > sodium > potassium. (b) With sodium, a little 2 : 3-dimethyl-2 : 3-diphenylbutane was formed at 130°, but none at 25°. (c) The reaction between *n*-butyl iodide and lithium at 95° gave a yield of 2 : 3-dimethyl-2 : 3-diphenylbutane per *n*-butyl group only slightly greater than that from the corresponding reaction between *n*-butyl iodide and *n*-butyl-lithium. (d) The reaction between *n*-butyl-lithium (2 mol.) and iodine (1 mol.) gave a yield of 2 : 3-dimethyl-2 : 3-diphenylbutane per *n*-butyl group almost identical with that from the corresponding reaction between equimolecular proportions of *n*-butyl-lithium and *n*-butyl iodide.

On the assumption (which is further discussed below) that, at a particular temperature, the yields of 2 : 3-dimethyl-2 : 3-diphenylbutane from the present reactions are related to the numbers of free *n*-butyl radicals which are formed, it is concluded from (a) that the order lithium > sodium > potassium is the order of decreasing tendency to produce these radicals. From (c) it is evident that the free radicals formed in the "lithium-Wurtz" reaction are very largely derived from a new type of homolytic reaction between alkyl-lithium compound and alkyl halide, rather than from a *direct* reaction between lithium and alkyl halide. This is a point of difference between Wurtz-type reactions in solution and the corresponding gas-phase reactions¹ and may be due to the fact that Wurtz reactions involve bulk metal, whereas the gas-phase reactions involve free metal atoms under conditions of low pressure and relatively high temperature where the possibility of capture of a free alkyl radical by a metal atom is much less. However, in the present reactions with *n*-butyl iodide, the fact that lithium appeared to give a slightly higher yield of 2 : 3-dimethyl-2 : 3-diphenylbutane than did *n*-butyl-lithium may indicate that a few additional free *n*-butyl radicals were formed in the former case by a direct reaction between the halide and the metal; but the difference in yields is too small to justify a definite conclusion. Identical yields of octane were obtained from these two experiments.

From (d), it appears that the initial reaction between *n*-butyl-lithium and iodine is : $n\text{-C}_4\text{H}_9\text{Li} + \text{I}_2 \longrightarrow n\text{-C}_4\text{H}_9\text{I} + \text{LiI}$. *n*-Butyl iodide may then react with a further mol. of *n*-butyl-lithium to produce free *n*-butyl radicals and other products. The hypothetical reaction, $n\text{-C}_4\text{H}_9\text{Li} + \frac{1}{2}\text{I}_2 \longrightarrow n\text{-C}_4\text{H}_9\cdot + \text{LiI}$, seems not to occur under the present conditions.

In the Wurtz reactions with sodium or potassium at 130°, analogy with the lithium reactions suggests that the very limited formation of free radicals arises from a homolytic reaction between alkyl-sodium or -potassium compound and alkyl halide. The mechanism could not be tested because alkyl-sodium and -potassium compounds are thermally unstable at 130° and would also rapidly metallate *isopropylbenzene*. These difficulties are less important at 25°, at which *n*-butyl iodide and sodium gave no indication of the formation of free radicals. The production of a trace of 2 : 3-dimethyl-2 : 3-diphenylbutane from a reaction between *n*-butyl iodide and *n*-butylsodium in *isopropylbenzene* at 25° was therefore unexpected. The anomaly may possibly arise from the unavoidable presence of mercury in the reaction mixture, and the result does not seriously affect the conclusion that no significant numbers of free *n*-butyl radicals were formed during the reactions between *n*-butyl iodide and sodium at 25°. The blue colour of the reaction mixture at 25° was rapidly discharged at 130°, but there was no detectable liberation of free radicals during this process. The colour may result from lattice defects in the sodium iodide crystals, possibly associated with a stoichiometric excess of sodium atoms, although its temperature stability was rather lower than expected.²¹

In all the cases where measurement was made, more butane than butene was formed, and the yields of butane exceeded the yields of 2 : 3-dimethyl-2 : 3-diphenylbutane. Both

²¹ Burns and Williams, *Nature*, 1955, **175**, 1043; Scott, Hrostowski and Bupp, *Phys. Rev.*, 1950, **79**, 341, 346.

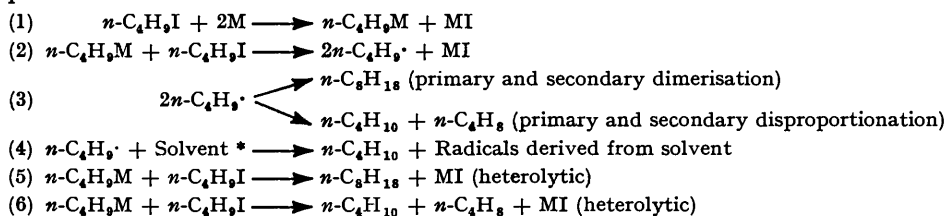
the disproportionation of free *n*-butyl radicals and a heterolytic elimination reaction between butyl halide and metal butyl should produce butane and butene in equal amounts. The observed preponderance of butane is superficially in accord with the belief that free butyl radicals abstract hydrogen from the solvent, but the probability of side reactions, e.g., $n\text{-C}_4\text{H}_9\text{Li} + \text{CH}_3\cdot\text{CH}_2\text{-CH}\cdot\text{CH}_2 \longrightarrow n\text{-C}_4\text{H}_{10} + \text{CH}_3\cdot\text{CHLi}\cdot\text{CH}\cdot\text{CH}_2$, and $n\text{-C}_4\text{H}_9\text{Li} \longrightarrow n\text{-C}_4\text{H}_8 + \text{LiH}$, blurs the significance of the butane:butene ratios.

It is next necessary to consider the quantitative significance of the yields of 2:3-dimethyl-2:3-diphenylbutane. First, it may be concluded from Kharasch, McBay, and Urry's results²² that the dimerisation of $\alpha\alpha$ -dimethylbenzyl radicals can occur almost quantitatively. These radicals have little or no tendency to disproportionate. Some combination of *n*-butyl and $\alpha\alpha$ -dimethylbenzyl radicals to give 2-methyl-2-phenylhexane may have occurred under the present conditions; but this hydrocarbon would also have resulted from a reaction between *n*-butyl halide and α -metallated *isopropyl*-benzene.

A further question is whether the butyl radicals reacted with the solvent to produce an equal number of $\alpha\alpha$ -dimethylbenzyl radicals. Two factors are important here: (a) the extent to which free butyl radicals dimerise and disproportionate under the present conditions, and (b) the possibility of a "cage effect" following the reaction, $\text{BuM} + \text{BuX} \longrightarrow 2\text{Bu}\cdot + \text{MX}$ (M = Li, Na, or K; X = Cl, Br or I).

Considering, first, under (a) those butyl radicals which were truly "free" in that they had escaped from any solvent cage, it is probable that at least 50% of them abstracted hydrogen from the solvent. This seems to follow from a result described in Part V¹⁵ where the photolysis of di-*n*-butylmercury in *isopropyl*benzene gave a 47% yield of 2:3-dimethyl-2:3-diphenylbutane and 2% of octane, together with unidentified material.

The importance of a "cage effect" is less easy to assess. The above considerations suggest that even the highest yields, ca. 20%, of 2:3-dimethyl-2:3-diphenylbutane correspond to the appearance of only ca. 40% of the butyl groups in the reagents as free butyl radicals. From the form of the reactions, it seems highly probable that butyl radicals are liberated in pairs: and if this is so, at the instant when such a pair is liberated by (say) the interaction of *n*-butyl bromide and *n*-butyl-lithium, the local concentration of *n*-butyl radicals must be greater than the mean concentration over the solution as a whole. Primary dimerisation and primary disproportionation will then be favoured until the radicals have diffused well apart, i.e., have become truly "free," or have reacted with the solvent. However, the possibility that a "cage effect" operates to produce the *bulk* of the usual products of Wurtz reactions is excluded with reasonable certainty because in disproportionation reactions between an alkylsodium compound RNa and an alkyl halide R'X, the greater part of the saturated hydrocarbon is derived from R, and the unsaturated hydrocarbon from R'.^{6, 14b} Also, there seems to be no obvious reason why radicals should be so much more effectively "caged" in the reactions of alkyl halides with RNa or RK compounds than in the corresponding reactions with RLi compounds.



* It is normal practice to employ diethyl ether as a solvent in Wurtz reactions. From the results of Kharasch and Urry,²³ it appears that diethyl ether is a rather more efficient trap for alkyl radicals than is *isopropyl*benzene, although the reaction products are less characteristic. Any radicals which might be formed during a Wurtz reaction in diethyl ether would therefore have an even smaller chance to dimerise and disproportionate.

²² Kharasch, McBay, and Urry, *J. Org. Chem.*, 1945, **10**, 401.

These considerations lead the writer to conclude that, in the Wurtz reactions which have now been studied, the usual coupling and disproportionation products are formed mainly by heterolytic reactions between metal alkyl and alkyl halide, and that the homolytic reaction with which these compete is only appreciable in extent when lithium is used. This view of the Wurtz reaction is expressed, for *n*-butyl iodide, in the equations (1)—(6) ($M = \text{Li, Na or K}$).

Further minor side reactions can include: (7) $n\text{-C}_4\text{H}_9\text{M} \longrightarrow n\text{-C}_4\text{H}_8 + \text{MH}$; metallation of butene from reactions (3), (6), and (7) by $n\text{-C}_4\text{H}_9\text{M}$; and attack on the solvent by $n\text{-C}_4\text{H}_9\text{M}$.

Coupling and disproportionation reactions between alkali-metal alkyls and alkyl halides have been widely investigated.¹⁴ The results have been interpreted in terms of heterolytic reactions in which the rate-determining step may vary from case to case:^{14c, e} the possibility of prior co-ordination between alkali-metal cation and halogen has been suggested. The possibility of a homolytic mechanism has been discussed by Morton and Cluff¹³ without direct experimental evidence*. The present results partially accord with their "radical-pair" hypothesis.†

The idea of competing homolytic and heterolytic reactions between two molecular species in the same environment implies that the corresponding transition states or complexes have comparable energies. The orientation of any two molecules at the moment of collision may, in part, decide which reaction path is followed. One might expect that free radicals would be most readily produced in straight-line collisions, *e.g.*, $\text{R-Li} \rightarrow \leftarrow \text{Br-R}$, where interaction between the alkyl groups is at a minimum. Also, loose co-ordination between metal and halogen might be a preliminary to homolysis of the R-Li and R-Br bonds. The induction period before precipitation of lithium halide may be significant in connection with the last suggestion.

The reactions between lithium or alkyl-lithium compounds and alkyl halides may have some practical value as sources of free alkyl radicals in solution. They have the merit of giving only one radical species at a time. Thus, when *n*-butyl radicals were generated in benzene from *n*-butyl bromide and *n*-butyl-lithium, the main products appeared to be aliphatic hydrocarbons which could not be separated; but infrared data indicated that a little *n*-butylbenzene was formed. No diphenyl was detected. The absence of solvent dimer is here not surprising in view of the relatively low reactivity of benzene towards many free radicals. It is also evident that *n*-butyl radicals add to benzene much less readily than do phenyl radicals.

The present investigations are being extended to the Fittig reaction, and to the use of metals outside Group I.

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* Kharasch and Urry²³ showed that free radicals are formed during the reactions between certain alkyl halides and alkylmagnesium bromides. They originally proposed a chain mechanism involving magnesium sub-bromide; but Kharasch and Reinmuth²⁴ have more recently given an alternative explanation that a direct homolytic reaction can occur, *viz.*, $\text{RMgX} + \text{RX} \longrightarrow 2\text{R}\cdot + \text{MgX}_2$. This suggestion appears very attractive in the light of the present results, where the question of catalysis by metal subhalide does not arise.

† Morton's further applications of this hypothesis to thermal decomposition¹³ and metallation reactions²⁵ of alkali-metal alkyls seem to be contradicted by the published evidence.^{15, 16, 26}

²³ Kharasch and Urry, *J. Org. Chem.*, 1948, **13**, 101.

²⁴ Kharasch and Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, 1954, p. 131.

²⁵ Morton, Claff, and Collins, *J. Org. Chem.*, 1955, **20**, 428; Morton and Claff, *ibid.*, p. 981.

²⁶ Bryce-Smith, Gold, and Satchell, *J.*, 1954, 2743; Gronowitz, *Arhiv Kemi*, 1954, **7**, 361; Gronowitz and Halvarson, *ibid.*, 1955, **8**, 343; Hall, Piccolini, and Roberts, *J. Amer. Chem. Soc.*, 1955, **77**, 4540.