# 403. *Alkali Organometal Compounds. Part I. The Reaction of Benzylsodium with Alkyl Halides.*

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A simple method for the preparation of pure alkylbenzenes is described, based on the reaction between benzylsodium and alkyl halides.

Modification of a previously described method for the preparation of benzylsodium has made it possible to obtain improved yields of alkylbenzenes by the reaction. Yields are higher than in the corresponding reaction using phenylsodium.

*p*-Xylene has been prepared by the interaction of *p*-tolylsodium with methyl iodide and methyl sulphate.

Refractive indices, densities, and boiling points have been determined for a number of pure alkylbenzenes.

Morton and his co-workers (*J. Amer. Chem. Soc.*, 1938, **60**, 1429; 1941, **63**, 327) prepared *n*-amylbenzene by the reaction sequence

$$n\text{-}C_5H_{11}Cl \xrightarrow[\text{benzene}]{\text{Na in}} C_6H_5Na \xrightarrow{\text{toluene}} C_6H_5{\cdot}CH_2Na \xrightarrow{n\text{-}C_4H_9Cl} C_6H_5{\cdot}C_5H_{11}$$

The reaction of *n*-alkyl chlorides with sodium in toluene was also shown to produce *n*-alkylbenzenes through the intermediate formation of benzylsodium.

A similar method has been used by Letsinger (*ibid.*, 1948, **70**, 406) to prepare optically active alkylbenzenes by the interaction of benzylsodium with (+)-2-bromobutane and (+)-2-bromooctane. *n*-Butyl and *n*-amyl chlorides were used for the preparation of benzylsodium, the yield being low in the former case.

As part of a programme of work on the preparation of pure hydrocarbons, we have studied the reaction of benzylsodium with a number of aliphatic halides. Benzylsodium prepared from *n*-amyl chloride as described by the above workers was considered unsuitable for the preparation of the lower alkylbenzenes in a pure state owing to the difficulty of complete separation from decane.

Gilman, Pacevitz, and Baine (*ibid.*, 1940, **62**, 1514) claimed to have obtained a 79% yield of benzylsodium, estimated as phenylacetic acid, by the interaction of chlorobenzene and sodium in toluene at 35°; the toluene suspension of phenylsodium obtained, heated under reflux for 3 hours, gave benzylsodium :

$$C_6H_5Na + C_6H_5{\cdot}CH_3 \longrightarrow C_6H_6 + C_6H_5{\cdot}CH_2Na$$

These have been reported as optimum conditions (Pacevitz, *J. Iowa State Coll. Acad. Sci.*, 1941, **16**, 117).

Using benzylsodium prepared by this method, we have obtained moderate yields of alkylbenzenes by interaction with primary and secondary halides. However, it has been found that the heating period of 3 hours for the preparation of benzylsodium is excessive, the reaction being, in fact, complete within 35 minutes at 105°. Moreover, in reactions with alkyl halides, benzylsodium prepared with the shorter heating period has given yields of alkylbenzenes approximately 15% higher, together with correspondingly decreased formation of tarry by-products. Reduction in the amount of toluene to half that used by Gilman *et al.* (*loc. cit.*) has not decreased yields.

We conclude that slow thermal decomposition of benzylsodium occurs at 105°.

Other experiments on the metallation of toluene have shown that approximately 25% formation of benzylsodium occurs when the suspension of phenylsodium in toluene is kept at room temperature for 20 hours. At 80°, conversion is almost complete after 1 hour.

Experiments with *n*-butyl halides have shown that temperature is an important factor in their reaction with benzylsodium. With the chloride and iodide, the highest yields of *n*-amylbenzene were obtained at 30°, whereas with the bromide the reaction was best performed at 105°. Approximately equal yields were obtained in each case. From the experimental point of view, the use of bromides was most convenient.

Secondary halides have likewise given good yields of the coupled product with benzylsodium. *tert.*-Butyl halides have given very small yields of phenyl*neo*pentane, not increased by working at −75°.

Normal coupling products have been obtained in good yields from allyl chloride and *cyclo*hexyl bromide. In the former case 4-phenylbut-1-ene was obtained free from isomeric unsaturated hydrocarbons.

For purposes of comparison, the reaction of ethyl and *n*-butyl bromides with phenylsodium has been examined. Yields of the coupled product have been found to be lower than in corresponding reactions using benzylsodium. This is in agreement with the observations of Morton (*loc. cit.*).

*n*-Butylbenzene prepared from phenylsodium has been found to be identical in physical properties with that prepared from benzylsodium. This excludes the possibilities of isomerisation or an *ortho*-reaction with benzylsodium.

Since benzylsodium is known to form ethylbenzene by its interaction with methyl sulphate (Morton, *J. Amer. Chem. Soc.*, 1940, **62**, 120) the reaction of phenylsodium with toluene-*p*-sulphonic esters was thought likely to prove an alternative route to alkylbenzenes. However, interaction of phenylsodium and *n*-butyl toluene-*p*-sulphonate gave a low yield of octane and no trace of the expected *n*-butylbenzene.

*Reactions with* p-*Tolylsodium.*—*p*-Tolylsodium is known to form benzylsodium slowly on long standing at room temperature (Bachmann and Clarke, *ibid.*, 1927, **49**, 2089) and more rapidly on heating (Gilman and Pacevitz, *ibid.*, 1940, **62**, 673). We have confirmed the latter authors' observation that interaction of *p*-chlorotoluene and sodium, followed immediately by treatment of the product with carbon dioxide, gives pure *p*-toluic acid and no phenylacetic acid.

By the interaction of *p*-tolylsodium and methyl iodide or methyl sulphate, *p*-xylene has been prepared in moderate yields. The yield of *p*-xylene from methyl sulphate was higher than the yield of *p*-toluic acid obtained from the reaction with carbon dioxide. This is of interest in view of the frequent use of the latter reaction for the estimation of organo-sodium compounds.

The absence of isomerisation and unsaturated by-products has made the reaction of these organo-sodium compounds with aliphatic halides very convenient for the preparation of pure alkylbenzenes. In the conditions used, the symmetrical Wurtz coupling product is formed in traces insufficient for its isolation and in most cases the required alkylbenzenes have been readily obtained pure by straightforward fractional distillation.

However, 2—3% of diphenyl is formed in the initial preparation of phenylsodium and, in the case of alkylbenzenes with a boiling point near to that of diphenyl, careful fractionation has been necessary in order to obtain pure products. The presence of traces of diphenyl is easily detected by refractive-index measurements.

Measurements of boiling points, refractive indices, and densities for hydrocarbons obtained in this work are recorded in Table II. The values have been found to be highly reproducible despite the fact that preparations have been on the relatively small scale of 0·5 g.-mol.

Where comparison is possible, the values are in close agreement with those obtained by Forziati, Norris, and Rossini (*J. Res. Nat. Bur. Stand.*, 1949, **43**, 473, 555) working with a series of specially purified hydrocarbons.

Agreement with the values give by Vogel (*J.*, 1948, 607) is less consistent.

Further work on the physical properties of alkylbenzenes is in progress and will be reported in a later paper.

## EXPERIMENTAL.

(All temperatures are corrected.)

Alkyl bromides were prepared from the corresponding refractionated alcohols by standard methods. Other halides were commercial products purified by shaking them with concentrated sulphuric acid, washing, drying, and distillation. All halides were refractionated before use, through a jacketed Fenske column with 35-cm. packed length and variable take-off (column A).

Benzene and toluene were sulphur-free. Light petroleum was freed from aromatic and unsaturated compounds by being shaken with 5% oleum, washed, dried, and distilled. All reagents were carefully dried.

The experimental conditions are illustrated by the following preparation of *n*-butylbenzene (any deviation is indicated in the notes to Table I).

A 1-l. flask was fitted with a dropping funnel, reflux condenser, wing-stirrer with mercury seal, thermometer, and gas inlet, all joints being of ground glass. In the flask were placed 300 c.c. of toluene and 27·5 g. (1·2 g.-at.) of sodium wire. The apparatus was filled with dry nitrogen and stoppered. At 30—35°, 68 g. (0·6 g.-mol.) of chlorobenzene were added dropwise during 2 hours, with vigorous stirring. Reaction started within a few minutes, the sodium surface becoming black, and was complete after a further 1½—2 hours at 30°.

The condenser was then fitted with a calcium chloride tube, and the mixture heated under reflux with stirring for 35 minutes. The reflux temperature, initially 107°, soon fell to 103° as benzene became formed by the exchange reaction. After removal of the heating bath, 49 g. (0·4 g.-mol.) of *n*-propyl bromide were added during 20 minutes at 103—105°.

After the mixture had cooled to room temperature, an excess of solid carbon dioxide was added to show the presence of unchanged benzylsodium. Water was finally added to destroy excess of sodium. The separated and dried toluene layer was distilled through column (A). No fraction corresponding to *n*-hexane was observed. After removal of most of the toluene through this column, the latter was replaced by a smaller one (B) of the same type with 8-cm. packed length.

The following fractions were collected at 765 mm. :

| No. | B. p. | $n_D^{20}$. | Wt., g. | No. | B. p. | $n_D^{20}$. | Wt., g. |
|---|---|---|---|---|---|---|---|
| (1) | 111—145° | 1·4930 | | (8) | 181·5° | 1·4903 | 2 |
| (2) | 145—170 | 1·4915 | 3 | (9) | 181·5—247 | — | 1·5 |
| (3) | 170—181·0 | 1·4901 | 4·5 | (10) | 247—275 | — | 1·5 |
| (4) | 181·0 | 1·4898 | 35·5 | (11) | 275—295 | — | 1·0 |
| (5) | 181·0—181·5 | 1·4898 | | | Residue | — | 6·5 |
| (6) | 181·5 | 1·4898 | | | | | |
| (7) | 181·5 | 1·4898 | | | | | |

Redistillation of (3) and (8) gave a further 4·5 g. of *n*-butylbenzene, b. p. 181·0—181·5°/765 mm., $n_D^{20}$ 1·4898. [At these rather high temperatures, a thermometer immersed in the vapour at the top of a fractionating column rarely records the true b. p. For this reason, refractive indices rather than b. p.s have been taken as criteria of purity. More accurate values for b. p.s have been obtained by using the Spencer–Cottrell apparatus (Table II).]

The total yield of pure *n*-butylbenzene was 40 g. (74%).

Acidification of the aqueous layer gave 3·9 g. of crude phenylacetic acid, m. p. 67—69°. Crystallisation from water gave 2·4 g. of m. p. 77°.

TABLE I.

*Yields of alkylbenzenes from the interaction of benzylsodium with halides.*

Yields of pure products (%; calculated on halides) from 0·6 g.-mol. of chlorobenzene, 1·2 g.-at. of sodium, and 0·4 g.-mol. of alkyl halides.

| | Reaction temp. | | | | Reaction temp. | | |
|---|---|---|---|---|---|---|---|
| Alkyl halide. | −70°. | 30°. | 70°. | 105°. | 30°. | 105°. | Product. |
| Ethyl bromide | — | — | — | 50 | — | — | *n*-Propylbenzene |
| *n*-Propyl bromide | — | — | — | 57 [c]; 60 [d] | — | 76; 74 [d] | *n*-Butylbenzene |
| *n*-Butyl chloride | — | 62 | 48 | 39 | — | — | *n*-Amylbenzene |
| *n*-Butyl bromide | — | 55 [e]; 54 | — | 67 | — | 79 ; 80 [h] | *n*-Amylbenzene |
| *n*-Butyl iodide | — | 65 | — | 60 | — | — | *n*-Amylbenzene |
| *n*-Amyl bromide | — | — | — | — | — | 73 | *n*-Hexylbenzene |
| 1-Bromo-3 : 5 : 5-trimethylhexane | — | — | — | 55 [f] | — | — | 1-*Phenyl*-4 : 6 : 6-*trimethylheptane* |
| *iso*Propyl bromide | — | — | — | 51 | — | — | *iso*Butylbenzene |
| *sec.*-Butyl bromide | — | 52 | — | 55 | — | 70 [d] | 1-Phenyl-2-methylbutane |
| *sec.*-Butyl chloride | — | — | — | — | 72 [h] | — | 1-Phenyl-2-methylbutane |
| *tert.*-Butyl chloride | — | 1·5 | — | 1·5 [i] | — | — | Phenyl*neo*pentane |
| *tert.*-Butyl bromide | 1·0 | 2·5 | — | — | — | — | Phenyl*neo*pentane |
| *cyclo*Hexyl bromide | — | — | — | — | — | 69 [g, h] | *cyclo*Hexylphenylmethane |
| Allyl chloride | — | 51 | — | — | 72 [d] | — | 4-Phenylbut-1-ene |

[a] Benzylsodium prepared by heating phenylsodium in toluene for 3 hrs. at 105° (Gilman *et al.*, *loc. cit.*). [b] Benzylsodium prepared by heating phenylsodium in toluene for 35 mins. at 105°. [c] Sodium powder was used instead of sodium wire in this experiment. Reaction with chlorobenzene was more difficult to initiate and proceeded more slowly. [d] Solid carbon dioxide was added to the reaction mixture before addition of water. Phenylacetic acid was obtained in each case. [e] 0·5 G.-mol. of *n*-butyl bromide used. [f] Owing to the proximity of the b. p. of 1-phenyl-4 : 6 : 6-trimethylheptane to that of diphenyl, there was considerable distillation loss on working up and the true yield was much higher. B. p. 96°/2·5 mm. (Found: C, 88·2; H, 11·9. $C_{16}H_{26}$ requires C, 88·0; H, 12·0%). *cyclo*Hexylphenylmethane was not obtained in a state of purity comparable with that of the other hydrocarbons in this series. Practically all of the product distilled at 130·0—130·5°/20 mm. and showed no unsaturation to bromine in carbon tetrachloride; $n_D^{20}$ 1·5245—1·5270. After being heated at 130° with sodium for several hours, the hydrocarbon had b. p. 122·5—123·0°/16 mm., $n_D^{20}$ 1·5258—1·5264. These variations in refractive index may have been due to the presence of traces of di*cyclo*hexyl. The p-*sulphonamide* formed colourless crystals (from light petroleum), m. p. 107·5° (Found: N, 5·4. $C_{13}H_{19}O_2NS$ requires N, 5·5%). Sidorova and Tsukervanik (*J. Gen. Chem. Russia*, 1941, **10**, 2073) give for *cyclo*hexylphenylmethane, b. p. 137°/20 mm., $n_D^{17}$ 1·5255. [h] In these experiments the amount of toluene was reduced from 300 c.c. to 150 c.c. (1·4 g.-mols.). The heating period at 100° for complete formation of benzylsodium was 50 mins. These are probably the best experimental conditions. Phenyl*neo*pentane was purified by being heated under reflux for several hours with alkaline permanganate; b. p. 185—186°. The p-*sulphonamide* formed colourless crystals (from light petroleum), m. p. 86° (Found: N, 6·3. $C_{11}H_{17}O_2NS$ requires N, 6·2%).

*Metallation of Toluene at Lower Temperatures.*—(1) *At* 25°. A suspension of phenylsodium in 300 c.c. of toluene prepared from 0·6 g.-mol. of chlorobenzene and 1·2 g.-atoms of sodium was stirred at 25° for

20 hours. At 30°, 55 g. (0·4 g.-mol.) of *n*-butyl bromide was added during 2 hours and the mixture stirred for 1 hour more. On working up and fractionating the product, 11 g. (19%) of *n*-amylbenzene were obtained, indicating approximately 25% formation of benzylsodium.

(2) *At* 80°. A suspension of phenylsodium in 300 c.c. of toluene was prepared from 0·6 g.-mol. of chlorobenzene and 1·2 g.-atoms of sodium and heated at 80° for 1 hour. 49 G. (0·4 g.-mol.) of *n*-propyl bromide was run in at 80° during 20 minutes and on cooling to room temperature, *ca.* 50 g. of solid carbon dioxide were added to the mixture. Water was added and, on distillation of the organic layer, no fraction corresponded to *n*-propylbenzene. However, it was not possible to obtain the normal sharp fraction corresponding to *n*-butylbenzene, the hydrocarbon obtained having a b. p. range of 178—181°/764 mm. and $n_D^{22\cdot5}$ 1·4884—1·4889 (35·5 g.).

Acidification of the aqueous liquor gave 1·5 g. of acids, m. p. 70—90°.

It was concluded that, under these conditions, the formation of benzylsodium was incomplete.

*Experiments with Phenylsodium.—Reaction with* n-*butyl bromide.* Phenylsodium was prepared from 27·5 g. (1·2 g.-atoms) of sodium wire and 68 g. (0·6 g.-mol.) of chlorobenzene in 300 c.c. of benzene under the conditions used previously with toluene as solvent. At 30°, 55 g. (0·4 g.-mol.) of *n*-butyl bromide were added during 2 hours with stirring. After a further hour at 30° water was added to decompose excess of sodium and phenylsodium. Distillation of the organic layer gave 30 g. (56%) of crude *n*-butylbenzene, b. p. 179—182°/751 mm., $n_D^{20}$ 1·4903, slightly unsaturated to bromine in carbon tetrachloride.

After heating of the crude product under reflux with sodium for 2 hours and refractionation (column B), 23·5 g. (44%) of *n*-butylbenzene were obtained, having b. p. 180—181°/751 mm., $n_D^{20}$ 1·4898, and saturated to bromine in carbon tetrachloride, and also 4·7 g. (7·5%) of diphenyl, m. p. 70°. This was the only experiment in which the formation of unsaturated matter was observed.

To find the effect of reaction temperature on the yield of *n*-butylbenzene, an experiment similar to the above was carried out with light petroleum (b. p. 100—120°) as solvent, addition of *n*-butyl bromide being made at 105° during 20 minutes. The yield of pure *n*-butylbenzene was 26·5 g. (49%).

*Reaction with ethyl bromide.* See also Acree (*Amer. Chem. J.*, 1903, **29**, 588). This experiment was carried out to check varying literature values for the refractive index of ethylbenzene.

A suspension of phenylsodium was prepared from 46 g. (2 g.-atoms) of sodium wire and 112·5 g. (1 g.-mol.) of chlorobenzene in 400 c.c. of light petroleum (b. p. 40—60°). 87 G. (0·8 g.-mol.) of ethyl bromide were added at 30° during 45 minutes and the mixture was stirred a further hour. Addition of water and normal working-up gave 42·5 g. (50%) of ethylbenzene showing no unsaturation with bromine in carbon tetrachloride and having $n_D^{20}$ 1·4958. The hydrocarbon, heated under reflux with sodium for 8 hours and refractionated (column A), had b. p. 134·4°/745 mm. and $n_D^{20}$ 1·4958.

*Reaction with* n-*butyl toluene*-p-*sulphonate.* To a suspension of phenylsodium prepared from 34 g. (0·3 g.-mol.) of chlorobenzene and 13·8 g. (0·6 g.-atom) of sodium wire in 150 c.c. of benzene were added 45·5 g. (0·2 g.-mol.) of freshly-distilled *n*-butyl toluene-*p*-sulphonate during 45 minutes at 50°. After the mixture had been kept overnight at room temperature, water was added and the separated organic layer fractionated. 1 G. of a liquid, b. p. 125—131°, was obtained, which was saturated to bromine in carbon tetrachloride, had $n_D^{20}$ 1·4140, and was thus probably *n*-octane.

No fraction corresponding to *n*-butyl benzene was observed.

*Experiments with* p-*Tolylsodium.—Reaction with carbon dioxide.* (Cf. Gilman and his co-workers, *J. Amer. Chem. Soc.*, 1940, **62**, 673, 1514.) *p*-Tolylsodium was prepared by addition of 12·6 g. (0·1 g.-mol.) of *p*-chlorotoluene during 2 hours to 4·6 g. (0·2 g.-atom) of sodium wire stirred in 50 c.c. of light petroleum (b. p. 40—50°) at 25° with the usual conditions for exclusion of air and moisture. The mixture was stirred for a further 2 hours at 25° and then rapidly poured on a large excess of solid carbon dioxide in a Dewar flask. Next morning water was added to destroy excess of sodium. Acidification of the aqueous layer gave 6·8 g. of *p*-toluic acid, almost pure without recrystallisation, m. p. 175°. Ether-extraction of the mother-liquor gave 0·15 g. of a brown acid, m. p. 161—163° without recrystallisation. From the odour, this contained traces of cresol. Phenylacetic acid was not found. The yield of *p*-toluic acid was 51%.

*Reaction with methyl iodide.* *p*-Tolylsodium was prepared, as in the previous experiment, from 50·5 g. (0·4 g.-mol.) of *p*-chlorotoluene and 23 g. (1 g.-atom) of sodium wire in 200 c.c. of light petroleum (b. p. 30—40°). 51 G. (0·36 g.-mol.) of methyl iodide were added at 30° during 30 minutes. Reaction was rapid. After a further 5 minutes' stirring, solid carbon dioxide was added to decolorise the solution. Excess of sodium was destroyed by addition of water. Fractionation at 745 mm. (column A) gave the following fractions :

| No. | B. p. | Wt., g. | M. p. | No. | B. p. | Wt., g. | M. p. |
|---|---|---|---|---|---|---|---|
| (1) | 90—120° | 1·0 | <0° | (5) | 136·0—136·5° | 1·9 | 12·0—12·3° |
| (2) | 120—132 | 1·5 | <0 | (6) | 136·5 | 14·2 | 12·3—12·7 |
| (3) | 132—135 | 1·0 | <0 | | Residue | 3 | — |
| (4) | 135—136 | 1·3 | 8·5—9·0 | | | | |

Fractions (5) and (6) represent a 42% yield of *p*-xylene. Fraction (6) had $n_D^{20}$ 1·49584.

The aqueous layer gave, on acidification, 2·85 g. (5·2%) of *p*-toluic acid, m. p. 175—176°, without recrystallisation.

*Reaction with methyl sulphate.* *p*-Tolylsodium was prepared, as in previous experiments, from 76 g. (0·6 g.-mol.) of *p*-chlorotoluene and 27·5 g. (1·2 g.-atoms) of sodium wire in 250 c.c. of light petroleum (b. p. 40—50°). At 30°, a mixture of 78·5 g. (0·625 g.-mol.) of methyl sulphate with 30 c.c. of benzene was added during 1 hour with vigorous stirring. The reaction mixture was then colourless. After addition of water, the organic layer was fractionated until the vapour temperature reached 90°. The crude *p*-xylene was then steam-distilled in the presence of potassium hydroxide. The dried steam-distillate was fractionated (column A) at 773 mm. and the following fractions were collected :

| No. | B. p. | Wt., g. | M. p. | No. | B. p. | Wt., g. | M. p. |
|---|---|---|---|---|---|---|---|
| (1) | 109—115° | 2·9 | <0° | (6) | 138·0—138·3° | 4·5 | 11·9—12·1° |
| (2) | 115—132 | 3·5 | <0 | (7) | 138·3—138·35 | 12·1 | 127·—12·8 |
| (3) | 132—136 | 2·0 | <0 | (8) | 138·35 | 11·4 | 12·6—12·8 |
| (4) | 136—137 | 2·4 | 7·5—8·5 | | Residue | 5·3 | — |
| (5) | 137—138 | 2·5 | 10·4—10·8 | | | | |

Distillation of the residue from a small flask without a column gave a further 4·2 g., m. p. 10·0—10·5°, b. p. 138—140° (fraction 9). Fractions (5)—(9) (37·1 g.) represent a 58% yield, based on *p*-chlorotoluene.

*Physical Properties.*—Data for the purest products obtained are given in Table II.

TABLE II.

| | B. p./ 760 mm. | $n_D^{20}$. | $d_4^{20}$. |
|---|---|---|---|
| Ethylbenzene | 136·1° | 1·49577 | 0·86709 |
| *p*-Xylene | 138·0 | 1·49579 | 0·86106 |
| *n*-Propylbenzene | 159·4 | 1·49186 | 0·86200 |
| *n*-Butylbenzene : | | | |
| (i) *ex* $C_6H_5{\cdot}CH_2Na$ | 182·9 | 1·48975 | 0·86017 |
| (ii) *ex* $C_6H_5Na$ | — | 1·48974 | 0·86017 |
| *iso*Butylbenzene | 172·7 | 1·48657 | 0·85345 |
| 4-Phenylbut-1-ene | 181·1° | 1·50748 | 0·88153 |
| *n*-Amylbenzene | 205·2 | 1·48827 | 0·85904 |
| 1-Phenyl-2-methylbutane | 196·1 | 1·48906 | 0·86072 |
| *n*-Hexylbenzene | 225·0 | 1·48698 | 0·85830 |
| 1-Phenyl-4 : 6 : 6-trimethylheptane | — | 1·48268 | 0·85591 |

Refractive indices were measured with a calibrated Pulfrich refractometer. Reproducibility with this instrument was ±0·00002 and values obtained with different samples came within these limits.

Densities are for the air-saturated hydrocarbons and are reduced to a vacuum. Individual measurements were reproducible within ±0·00003 g./ml.

B. p.s were measured with the Spencer–Cottrell apparatus and were reproducible within ±0·2°.

All measurements were made with hydrocarbons freshly distilled over sodium or potassium. Slight deterioration, probably by oxidation, was observed when samples were kept in stoppered bottles for some months.

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