

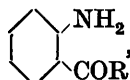
CCXVI.—*Studies in the n-Butyl Series. Part I.*
Aryl n-Propyl Ketones.

By GILBERT T. MORGAN and WILFRED JOHN HICKINBOTTOM.

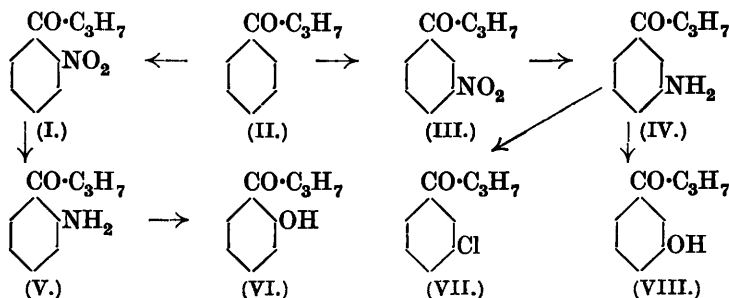
THE industrial development during recent years of a fermentation yielding *n*-butyl alcohol has rendered available considerable amounts of this alcohol, for which sufficient use has not hitherto been found. A consideration of the problem of the utilisation of this product leads to the conclusion that the solution lies in the employment of derivatives of *n*-butyl alcohol rather than in its use as a substitute for fusel oil. It is from this point of view that we have examined the properties of certain *n*-butyl compounds derived by practicable processes from *n*-butyl alcohol.

The influence of butyl and butyryl groups in enhancing the odour of chemical substances is well known, and aryl derivatives containing these osmophoric radicles have been prepared and examined. On comparing the odours of the substituted *n*-butylbenzene with those of the corresponding derivatives of phenyl *n*-propyl ketones, it is noticed that the odour diminishes in intensity on passing from the hydrocarbon to the ketone. This is particularly noticeable with the nitro-derivatives. *3-Nitrophenyl n-propyl ketone*, for instance, is almost inodorous, whilst the nitro-*n*-butylbenzenes and *2-nitro-1 : 4-di-n-butylbenzene* have characteristic odours. Orientation has its effect, for *2-nitrophenyl n-propyl ketone* has a pleasant odour, which is, however, less fragrant than that of the corresponding nitro-derivative of *n*-butylbenzene.

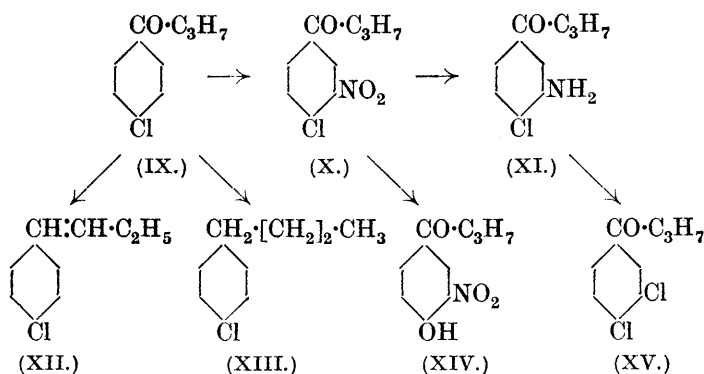
This contrast is not in accordance with the osmophoric theory of Rupe and Majewski (*Ber.*, 1900, **33**, 3401; compare also Klimont, "Die Synthetische und Isolierten Aromatica"), for it might be expected that the presence of two osmophores, $\text{—CO}\cdot\text{CH}_2\text{—}$ and —NO_2 , would give rise to a substance having an odour at least as intense as that of the nitrohydrocarbon. This anomaly is explicable on the assumption that in the aromatic series the effect of an osmophoric grouping is variable, depending, among other factors, on the presence of other osmophores in the molecule and also on their relative positions, so that the odour of a compound containing more than one osmophoric group in its molecule may be either increased or diminished as the orientation of the substituent varies. This influence of orientation is illustrated by a comparison of the odours of various derivatives of phenyl *n*-propyl ketone. Substitution in the *meta*-position yields, as a rule, substances with faint odours, whilst the corresponding *ortho*-compounds generally possess powerful and characteristic odours. It is noteworthy that 2-aminophenyl *n*-propyl ketone, which is an odoriferous substance, contains the grouping characteristic of methyl anthranilate,

, where $\text{R} = \text{C}_3\text{H}_7$ or $\cdot\text{O}\cdot\text{CH}_3$ (compare Rupe and Majewski, *Ber.*, 1900, **33**, 3401).

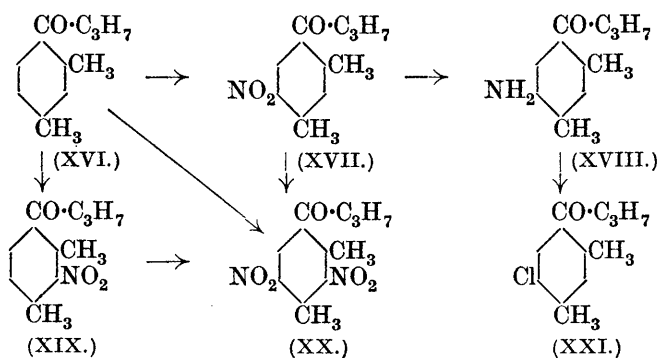
Butyryl chloride was condensed in turn with benzene, chlorobenzene, and *m*-xylene; the resulting ketones were converted successively into their nitro- and amino-derivatives. In the case of phenyl *n*-propyl ketone (II) nitration follows the *meta*-law of substitution, the *meta*-nitro-compound (III) is the main product, but the formation of a small proportion of the *ortho*-nitro-derivative (I) was noticed.



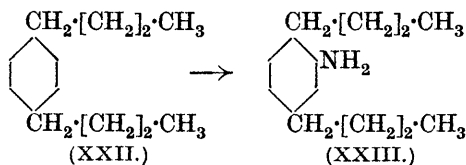
With *p*-chlorophenyl *n*-propyl ketone (IX) the nitro-group enters exclusively the *ortho*-position with respect to chlorine, yielding 4-chloro-3-nitrophenyl *n*-propyl ketone (X).



In the case of *m*-4-xylyl *n*-propyl ketone (butyro-2 : 4-dimethylphenone, XVI), nitration occurs as with the parent aromatic hydrocarbon, *m*-xylene; the main product is 6-nitro-*m*-4-xylyl *n*-propyl ketone (XVII), whereas 2-nitro-*m*-4-xylyl *n*-propyl ketone (XIX) is formed in smaller proportion. Further nitration leads to 2 : 6-dinitro-*m*-4-xylyl *n*-propyl ketone (XX).



In the foregoing condensations to form mixed ketones the introduction of the butyryl group into the benzene ring through the agency of the Friedel and Crafts reaction occurs much more smoothly than the substitution of a butyl group for chlorine by the Fittig reaction in the formation of *p*-di-*n*-butylbenzene (XXII) from *p*-dichlorobenzene.



Accordingly, the mixed ketones have been submitted to a more detailed examination.

EXPERIMENTAL.

I. *Phenyl n-Propyl Ketone*.

Phenyl *n*-propyl ketone was prepared in a 69 per cent. yield by the interaction of *n*-butyryl chloride* and an excess of benzene in presence of aluminium chloride. Phenyl *n*-propyl ketone was characterised by its *p*-nitrophenylhydrazone, which separated from glacial acetic acid in orange-red, prismatic needles having a metallic blue reflex; it melted at 163° (Found: N = 15.13. $C_{16}H_{17}O_2N_3$ requires N = 14.84 per cent.).

1. *Nitration in Acetic Anhydride*. 3-Nitrophenyl *n*-Propyl Ketone (III).—Phenyl *n*-propyl ketone (5.2 grams) was cautiously added with continuous stirring to 33 grams of fuming nitric acid mixed with 32 grams of acetic anhydride, the temperature being maintained below 5°. After half an hour, the nitration mixture was poured on to crushed ice, when crude 3-nitrophenyl *n*-propyl ketone was precipitated as a white, curdy solid, which was pressed from oily by-products. The nitrated ketone separated from warm alcohol in white, brittle plates melting at 61° (Found: C = 61.73; N = 7.53. $C_{10}H_{11}O_3N$ requires C = 62.15; N = 7.25 per cent.). It was not readily soluble in light petroleum or cold alcohol, but more readily so in ether or chloroform. 3-Nitrophenyl *n*-propyl ketone was oxidised to *m*-nitrobenzoic acid on heating with chromic acid or potassium permanganate in presence of dilute sulphuric acid; it yielded a *phenylhydrazone* crystallising from alcohol in orange-red masses of small needles melting at 103°. The *p*-nitrophenylhydrazone was deposited from warm glacial acetic acid in minute, pale yellow crystals melting at 205° (Found: N = 17.28. $C_{16}H_{16}O_4N_4$ requires N = 17.07 per cent.).

2-Nitrophenyl *n*-Propyl Ketone (I).

The oily filtrates and washings from the 3-nitro-compound were repeatedly extracted with ether to remove the liquid product of the nitration. The ethereal extract was washed with aqueous sodium hydroxide solution and the solvent evaporated. The residual oil contained a mixture of the 2- and 3-nitro-compounds, from which the greater part of the solid isomeride was removed by freezing. There was not sufficient material available to attempt

* Our thanks are due to Captain Desborough, of the Royal Naval Cordite Factory, for the *n*-butyl alcohol required in this investigation.

the lengthy fractionation under diminished pressure which appeared necessary to isolate the *ortho*-nitro-compound in a pure state, and recourse was made to the difference in behaviour of the isomerides with *p*-nitrophenylhydrazine. Crude 2-nitrophenyl *n*-propyl ketone was heated in a boiling water-bath with three-fifths of its weight of *p*-nitrophenylhydrazine in alcoholic solution. A dark red oil resulted which slowly deposited the *p*-nitrophenylhydrazone of the 3-nitro-compound as a reddish-yellow solid. The separation was hastened by treatment with dry ether, when, on submitting the residue to distillation in a current of steam, a pale yellow oil passed over, which was subjected to further treatment with *p*-nitrophenylhydrazine. It was finally purified by two steam distillations in presence of dilute hydrochloric acid. By these means 2-nitrophenyl *n*-propyl ketone was obtained as a pale yellow oil having a sweet odour resembling to some extent that of nitrobenzene (Found: $N = 7.01$. $C_{10}H_{11}O_3N$ requires $N = 7.25$ per cent.).

In the nitration of phenyl *n*-propyl ketone with nitric acid and acetic anhydride, the yield of mixed nitro-compounds after removing isonitroso-compounds and oxidation products amounted to 97—98 per cent. of the calculated amount.

2. *Nitration in Sulphuric Acid*.—A mixture of 1.1 to 1.2 molecular proportions of nitric acid (d 1.42) and concentrated sulphuric acid (18 grams) was added with continuous stirring to phenyl *n*-propyl ketone (5.4 grams) dissolved in 60 grams of concentrated sulphuric acid, the temperature being maintained below 5° throughout the operation. The mixture was left at 0° for about two hours and then poured on to ice. The isolation of 3-nitrophenyl *n*-propyl ketone was effected as in the preceding preparation.

3-Aminophenyl *n*-propyl ketone (IV), obtained in good yield by the reduction of the corresponding nitro-compound with zinc dust and ammonium chloride in aqueous alcoholic solution, was purified by fractionation under diminished pressure; it distilled over as a pale yellow, viscous oil at $194\text{--}197^\circ/29\text{--}30$ mm. and solidified to a white mass of crystals melting at $27\text{--}28^\circ$ (Found: $N = 8.30$. $C_{10}H_{13}ON$ requires $N = 8.59$ per cent.).

The *hydrochloride* separated from its concentrated solution in hydrochloric acid in masses of colourless needles, but was hydrolysed in aqueous solution. The *zincichloride* was precipitated as a white, sparingly soluble mass by the addition of an aqueous solution of zinc chloride to a suspension of the base. The *picrate* separated from warm benzene in bright yellow nodules or rosettes of needles melting at $132\text{--}133^\circ$ (Found: $N = 14.44$. $C_{10}H_{13}ON, C_6H_3O_7N_3$ requires $N = 14.28$ per cent.).

3-Acetylaminophenyl *n*-propyl ketone, prepared by warming the

base with acetic anhydride, separated from a mixture of benzene and light petroleum in plates melting at $71.5-72.5^{\circ}$ (Found : $N = 7.02$. $C_{12}H_{15}O_2N$ requires $N = 6.83$ per cent.).

3-Benzoylamino-phenyl n-propyl ketone separated from warm aqueous alcohol in small, white crystals melting at $103-104^{\circ}$ (Found : $N = 5.17$. $C_{17}H_{17}O_2N$ requires $N = 5.24$ per cent.).

n-Butyrophenone-3-azo- β -naphthol, obtained by coupling 3-diazo-phenyl *n*-propyl ketone chloride with β -naphthol in alkaline solution, crystallised from warm alcohol in small, red needles having a faint green reflex (m. p. $127-128^{\circ}$) (Found : $N = 9.05$. $C_{20}H_{18}O_2N_2$ requires $N = 8.80$ per cent.). It gave a crimson coloration in concentrated sulphuric acid.

n-Butyrophenone-3-azo- β -naphthylamine, produced as in the preceding preparation, using an alcoholic solution of β -naphthylamine, crystallised from warm glacial acetic acid in orange-red plates or scales having a coppery lustre, or on slow cooling in small, acicular plates arranged in clusters. It melted at $149-150^{\circ}$ (Found : $N = 13.51$. $C_{20}H_{19}ON_3$ requires $N = 13.25$ per cent.). This *azo- β -naphthylamine* developed in concentrated sulphuric acid a violet-blue coloration, changing to red and brown on dilution. Concentrated hydrochloric acid in glacial acetic acid gave rise to a bright red coloration.

n-Butyrophenone-3-azoresorcinol.—The diazotised amino-ketone was coupled with resorcinol in either aqueous or alcoholic solution in presence of sodium acetate, when the crude *azo*-compound separated. It was purified by precipitation from its solution in dilute sodium hydroxide and finally by crystallisation from warm benzene, when it separated as an orange-red powder melting at 144° (Found : $N = 10.10$. $C_{16}H_{16}O_3N_2$ requires $N = 9.86$ per cent.). A small amount of another *azo*-compound was obtained, which was insoluble in aqueous alkalis, but soluble in alcoholic potassium hydroxide. It separated from alcohol as a bright red, sparingly soluble powder. Sulphuric acid developed a red coloration.

3-Hydroxyphenyl n-Propyl Ketone (VIII).—On boiling the diazotised solution from 3-aminophenyl *n*-propyl ketone with an excess of diluted sulphuric acid, *3-hydroxyphenyl n-propyl ketone* separated as a dark oil, becoming solid on cooling; it was purified by solution in dilute sodium hydroxide and precipitation with acid, followed by crystallisation from warm light petroleum. It crystallised from a mixture of benzene and light petroleum in white, rhombic plates melting at 63° (Found : $C = 73.10$; $H = 7.46$. $C_{10}H_{12}O_2$ requires $C = 73.13$; $H = 7.38$ per cent.). *3-Hydroxyphenyl n-propyl ketone*, which has only a faint, pleasant, phenolic odour, coupled with diazotised *p*-nitroaniline to yield a red *azo*-compound.

The *p*-nitrophenylhydrazone of 3-hydroxyphenyl *n*-propyl ketone crystallised from benzene in orange-yellow needles melting at 160° (Found: N = 14·17. $C_{16}H_{17}O_3N_3$ requires N = 14·04 per cent.).

3-Chlorophenyl *n*-propyl ketone (VII), an almost colourless oil volatile in steam, was obtained from the corresponding amino-compound by the Sandmeyer reaction. Its odour resembled that of 4-chlorophenyl *n*-propyl ketone (IX), but was less intense (Found: Cl = 19·15. $C_{10}H_{11}OCl$ requires Cl = 19·42 per cent.).

The *p*-nitrophenylhydrazone separated from glacial acetic acid in minute, dull yellow crystals melting at 138° (Found: N = 13·58. $C_{16}H_{16}O_2N_3Cl$ requires N = 13·23 per cent.).

2-Aminophenyl *n*-Propyl Ketone (V).—By reducing 2-nitrophenyl *n*-propyl ketone (I) with zinc dust and ammonium chloride in boiling alcoholic solution, this amine was obtained as a pale yellow oil, volatile in steam and possessing a characteristic and pleasant odour when dilute. On adding concentrated hydrochloric acid to the base, the hydrochloride separated in clusters of white, prismatic needles melting at 160—162° to a dark red liquid. It darkened a few degrees below its melting point (Found: N = 6·95; Cl = 17·75. $C_{10}H_{13}ON, HCl$ requires N = 7·01; Cl = 17·76 per cent.). The amine was readily obtained by the reduction of the liquid product of the nitration of phenyl *n*-propyl ketone. On distilling the mixture of amines in a current of steam, the *ortho*-compound passed over the more readily, and was obtained pure by crystallising its hydrochloride two or three times from concentrated hydrochloric acid.

The amine was diazotised readily in dilute hydrochloric acid solution, and on pouring the solution of the diazonium salt into alkaline β -naphthol the *azo*- β -naphthol separated as a bright red powder, which crystallised from warm alcohol in bright red masses of small crystals having a faint metallic reflex. It melted at 154—155° (Found: N = 9·10. $C_{20}H_{18}O_2N_2$ requires N = 8·80 per cent.). The *azo*-compound developed a violet coloration in concentrated sulphuric acid.

On boiling a solution of the diazotised amine with excess of dilute sulphuric acid, 2-hydroxyphenyl *n*-propyl ketone (VI) separated as a pale yellow, viscous liquid, which was purified by solution in alkali followed by distillation in a current of steam (Found: C = 73·24; H = 7·13. $C_{10}H_{12}O_2$ requires C = 73·13; H = 7·39 per cent.).

II. 4-Chlorophenyl *n*-Propyl Ketone (IX).

n-Butyryl chloride (30 grams) was added gradually with continuous stirring to 83 grams of chlorobenzene mixed with freshly-prepared aluminium chloride (35 grams), the temperature being

maintained at 40—60°. After four hours, the product was poured on to ice and the pale yellow oil, having been washed with aqueous sodium hydroxide solution, was distilled, when it gave a colourless fraction at 253—254° (uncorr.) which solidified on cooling to a mass of crystalline and practically pure 4-chlorophenyl *n*-propyl ketone (yield 72 per cent.); this product separated from alcoholic solution in white, soft, tabular crystals melting at 36° (Found : Cl = 19.29. $C_{10}H_{11}OCl$ requires Cl = 19.42 per cent.). The ketone, which was soluble in the common organic media, was characterised by a pleasant odour more powerful than that of phenyl *n*-propyl ketone.

Oxidation of 4-chlorophenyl *n*-propyl ketone with sodium dichromate and dilute sulphuric acid gave *p*-chlorobenzoic acid, thereby establishing the orientation of the chlorine substituent with respect to the ketonic group.

The phenylhydrazone crystallised from alcohol in white, slender needles melting at 85° (Found : N = 9.20. $C_{16}H_{17}N_2Cl$ requires N = 10.27 per cent.). This hydrazone was found to be unstable, a pure specimen becoming converted into a dark brown tar after one month in a closed tube.

The *p*-nitrophenylhydrazone separated from a mixture of benzene and alcohol in small, yellow crystals melting at 173—174° (Found : N = 13.39. $C_{16}H_{16}O_2N_3Cl$ requires N = 13.23 per cent.).

Reduction of 4-Chlorophenyl n-Propyl Ketone.

(a) 4-Chloro-*n*-butylbenzene.—The reduction was carried out at 80—100° with hydrochloric acid and amalgamated zinc, according to Clemmensen's method for the reduction of ketones to hydrocarbons (*Ber.*, 1913, **46**, 1838). After twelve hours, the insoluble, yellow oil was removed and distilled in a current of steam. In the distillate crude 4-chloro-*n*-butylbenzene (XIII) was obtained, which was fractionally distilled after being separated and dried. The main distillate was collected at 225—228°/761 mm. as a colourless, refractive liquid stable to cold neutral permanganate solution and possessing a powerful odour of anise (Found : Cl = 20.72. $C_{10}H_{13}Cl$ requires Cl = 21.03 per cent.).

4-Chlorobutenylbenzene (XII).—In the reduction of the ketone by Clemmensen's method a small quantity of an unsaturated compound was usually obtained, the yield of which was increased by continuing the reduction for a shorter period or by working at a lower temperature. Under these conditions a mixture of 4-chlorobutenylbenzene and 4-chloro-*n*-butylbenzene was obtained in the fraction distilling between 225° and 240°. As the difference in the boiling points of the two substances was inconsiderable, and

as the quantity of available material did not permit of a systematic fractionation, evidence of the presence in the mixture of 4-chlorobutenylbenzene was obtained by converting the compound into its dibromide. That portion of the crude reaction product which was volatile in steam was suspended in water and treated with bromine until there was no further absorption. The heavy oil which resulted, having been treated with sodium sulphite solution, was distilled in steam, when a pasty, non-volatile residue (*b*) was obtained on cooling. The liquid portion volatile in steam was separated by distillation into 4-chloro-*n*-butylbenzene (*a*) and a liquid (*c*) boiling with decomposition above 230° and having a fragrant odour of hyacinths. Since the liquid (*c*) contained bromine and yielded 4-chlorobutenylbenzene on boiling with anhydrous pyridine for seven hours, it was probably 4-chlorobromobutylbenzene.

4-Chlorobutenylbenzene, a colourless, refractive liquid boiling at 234—237°/749 mm., had an odour resembling that of the saturated hydrocarbon (*a*), except that it was less pronounced and somewhat alliaceous (Found: Cl = 21.16. $C_{10}H_{11}Cl$ requires Cl = 21.28 per cent.).

(*b*) 4-Chloro- $\alpha\beta$ -dibromo-*n*-butylbenzene.—The pasty residue (*b*) obtained in the foregoing steam distillation was drained and crystallised from alcohol, when the purified dibromide separated in transparent prisms melting at 72° (Found: $AgCl + AgBr = 159.6$. $C_{10}H_{11}ClBr_2$ requires $AgCl + AgBr = 159.0$ per cent.).

The reduction of 4-chlorophenyl *n*-propyl ketone with amalgamated zinc and hydrochloric acid gave a varying proportion of a vitreous residue, not volatile in steam. By substituting for aqueous hydrochloric acid a solution of one part of concentrated hydrochloric acid in two parts of alcohol, the amount of by-product was increased. The substance was only sparingly soluble in alcohol, but more readily so in benzene or light petroleum. It melted indefinitely at 55—60° and was presumably a *polymeride* of 4-chlorobutenylbenzene.

4-Chloro-3-nitrophenyl *n*-Propyl Ketone (X).—It was found necessary to carry out the nitration of 4-chlorophenyl *n*-propyl ketone at a temperature not exceeding -5° , in order to reduce the tendency to oxidation.

4-Chlorophenyl *n*-propyl ketone (2 grams) dissolved in 18 grams of sulphuric acid (d 1.84) was cautiously added to a mixture of 15 grams of nitric acid (d 1.42) and 36 grams of concentrated sulphuric acid, cooled to -12° and constantly stirred. After the ketone had been added, the nitration mixture was left for a period of ten to thirty minutes and then poured on to crushed ice. The white, curdy solid, after being washed with water and sodium

carbonate solution, was purified by crystallisation from alcohol, when it separated in white plates melting at 53° (Found : N = 6.34; Cl = 15.25. $C_{10}H_{10}O_3NCl$ requires N = 6.15; Cl = 15.58 per cent.).

4-Chloro-3-nitrophenyl *n*-propyl ketone was faintly odorous, and was sparingly soluble in light petroleum or cold alcohol, but dissolved more readily in ether. On oxidation with aqueous chromic acid solution in presence of sulphuric acid, 4-chloro-3-nitrobenzoic acid (m. p. 180°) was obtained.

The phenylhydrazone separated from alcohol in acicular, golden yellow crystals melting at $116-117^{\circ}$ (Found : N = 12.91. $C_{16}H_{16}O_2N_2Cl$ requires N = 13.23 per cent.).

The *p*-nitrophenylhydrazone, obtained as a bright yellow, crystalline powder, melted at 215° (Found : N = 15.53. $C_{16}H_{15}O_4N_4Cl$ requires N = 15.45 per cent.).

On heating 4-chloro-3-nitrophenyl *n*-propyl ketone with phosphoric acid at $150-160^{\circ}$, no evidence was obtained of the fission of the butyryl group, the bulk of the substance being recovered unchanged (compare Klages and Lickroth, *Ber.*, 1899, **32**, 1563), excepting for a trace of 3-nitro-4-hydroxyphenyl *n*-propyl ketone (XIV), which was obtained more readily on heating the nitrochloro-compound with eighty times its weight of 6 per cent. aqueous potassium hydroxide solution. This nitrophenolic substance was obtained from boiling light petroleum in pale yellow needles melting at 46° (Found : N = 6.71. $C_{10}H_{11}O_4N$ requires N = 6.70 per cent.); it was readily soluble in the ordinary organic solvents with the exception of light petroleum.

The *p*-nitrophenylhydrazone, separating from glacial acetic acid in masses of orange crystals, melted at $203-204^{\circ}$ (Found : N = 16.50. $C_{16}H_{16}O_5N_4$ requires N = 16.27 per cent.).

4-Chloro-3-aminophenyl *n*-propyl ketone (XI), obtained in good yield by the reduction of the corresponding nitro-compound in alcoholic solution with zinc dust and a trace of ammonium chloride, crystallised from alcohol or warm light petroleum in white, shining plates melting at 97° (Found : N = 7.37. $C_{10}H_{12}ONCl$ requires N = 7.09 per cent.).

The hydrochloride separated from warm dilute hydrochloric acid in colourless needles, sparingly soluble in water (Found : HCl = 15.23. $C_{10}H_{12}ONCl, HCl$ requires HCl = 15.58 per cent.).

The diazo-solution from the foregoing hydrochloride, when poured into alkaline β -naphthol, yielded the red azo- β -naphthol, which crystallised from glacial acetic acid in red, prismatic needles having a green reflex (m. p. 153°) and developed a reddish-purple coloration with concentrated sulphuric acid (Found : N = 8.16. $C_{20}H_{17}O_2N_2Cl$ requires N = 7.94 per cent.).

3 : 4-Dichlorophenyl *n*-propyl ketone (XV), prepared from 4-chloro-3-aminophenyl *n*-propyl ketone by the Sandmeyer reaction, was isolated by distillation in steam and obtained as a colourless oil which could not be induced to crystallise. The odour of this compound was faintly reminiscent of anise and resembled that of 4-chlorophenyl *n*-propyl ketone, although not so intense. 3 : 4-Dichlorophenyl *n*-propyl ketone was characterised by its *p*-nitrophenylhydrazone, which separated from warm glacial acetic acid in bright yellow, prismatic needles melting at 183° (Found : N = 12.10. $C_{16}H_{15}O_2N_3Cl_2$ requires N = 11.94 per cent.).

III. *m*-4-Xylyl *n*-Propyl Ketone (XVI).

The following method of preparation gave a better yield of the ketone than that obtained by previous workers (Claus, *J. pr. Chem.*, 1891, [ii], **43**, 532; Klages, *Ber.*, 1902, **35**, 2257).

A small quantity of *n*-butyryl chloride was added to a mixture of *m*-xylene (34.6 grams) and aluminium chloride (27 grams). After the mixture had been warmed to 60° and an evolution of hydrogen chloride had commenced, further amounts of the acyl chloride were gradually added, the temperature being maintained at 50–60°. When all the *n*-butyryl chloride, amounting to 21.7 grams, had been added, the reaction was allowed to proceed at 50–60° with constant agitation for three hours, then at the ordinary temperature for a period of twelve hours and finally at 60° for three hours. The product, after being poured into water and washed with dilute sodium hydroxide solution, was dried and fractionally distilled. A fraction amounting to 26.25 grams was collected between 252° and 259°, and on repeated fractionation 23 grams of pure *m*-4-xylyl *n*-propyl ketone were obtained boiling at 258–259°/760 mm.; 9.95 grams of *m*-xylene were recovered, the yield of pure ketone amounting to 64 per cent. of the theoretical. *m*-4-Xylyl *n*-propyl ketone gave a *p*-nitrophenylhydrazone, which separated from alcohol in small, bright yellow crystals melting at 102–103° (Found : N = 13.79. $C_{18}H_{21}O_2N_3$ requires N = 13.50 per cent.).

6-Nitro-*m*-4-xylyl *n*-Propyl Ketone (XVII).—The introduction of one nitro-group into *m*-4-xylyl *n*-propyl ketone was effected by dissolving the ketone (8.8 grams) in twelve times its weight of concentrated sulphuric acid and, after cooling to 0°, adding slowly a mixture of 4.5 grams of nitric acid (*d* 1.42) and 36 grams of concentrated sulphuric acid. During the nitration the temperature was kept below 15° and the mixture stirred continuously for about two hours after all the nitric acid had been added. It was then

poured on to crushed ice. The precipitated, semi-solid product was removed, and after it had been cooled to -10° and filtered at a low temperature there remained an almost white solid, which was washed successively with dilute sodium carbonate solution and water. It crystallised from warm alcohol in masses of slender, bayonet-shaped needles melting at $59-60^{\circ}$ (Found: C = 65.2; H = 6.66; N = 6.43. $C_{12}H_{15}O_3N$ requires C = 65.13; H = 6.83; N = 6.33 per cent.).

6-Nitro-m-4-xylyl n-propyl ketone was only moderately soluble in cold alcohol, but more readily so in chloroform, light petroleum, or glacial acetic acid. On oxidation with an aqueous solution of chromic acid in presence of dilute sulphuric acid, 5-nitro-2:4-dimethylbenzoic acid was obtained, melting at $194-195^{\circ}$ (Claus, *J. pr. Chem.*, 1890, [ii], **41**, 495, gives m. p. 195° [uncorr.]; Ahrens, *Annalen*, 1892, **271**, 18, gives m. p. $196-197^{\circ}$).

2-Nitro-m-4-xylyl n-Propyl Ketone (XIX).—The liquid product of the nitration, after being washed with sodium carbonate solution and water, deposited appreciable amounts of the 6-nitro-compound when cooled to -15° , and further quantities of the solid isomeride were removed by extracting the oily portion with small quantities of alcohol. After a prolonged treatment with alcohol at temperatures below 0° , an oil was obtained which did not solidify at -15° (Found: N = 6.42. $C_{12}H_{15}O_3N$ requires N = 6.33 per cent.). The oil, however, was not pure, for on oxidation a mixture of nitrodimethylbenzoic acids was obtained.

6-Amino-m-4-xylyl n-propyl ketone (XVIII), obtained by the reduction of the nitro-compound with zinc dust and ammonium chloride in alcoholic solution, separated from warm light petroleum in hard, almost colourless, hexagonal prismatic needles melting at 56° (Found: N = 7.44. $C_{12}H_{17}ON$ requires N = 7.33 per cent.). The *hydrochloride* crystallised from warm dilute hydrochloric acid in white, slender, acicular crystals (Found: Cl = 15.61. $C_{12}H_{17}ON, HCl$ requires Cl = 15.58 per cent.). The *sulphate* separated from water in long, fern-like crystals.

Acetylation with acetic anhydride yielded *6-acetyl-amino-m-4-xylyl n-propyl ketone*, crystallising from petroleum (b. p. $80-100^{\circ}$) in a white, tangled mass of needles melting at 123° (Found: N = 6.35. $C_{14}H_{19}O_2N$ requires N = 6.01 per cent.). This amine, diazotised in dilute hydrochloric acid and coupled with alkaline β -naphthol, gave *butyro-2:4-dimethylphenone-5-azo- β -naphthol*, which crystallised from warm glacial acetic acid in bright red masses of slender needles and had a faint, green reflex (m. p. $194-195^{\circ}$) (Found: N = 8.44. $C_{22}H_{22}O_2N_2$ requires N = 8.09 per cent.). The azo-derivative was sparingly soluble in cold alcohol or

glacial acetic acid, but dissolved more readily in chloroform; it dissolved in concentrated sulphuric acid to a reddish-purple solution.

6-Chloro-m-4-xylyl n-Propyl Ketone (XXI).—The replacement of the amino-group by chlorine was effected by the Sandmeyer reaction. This chloro-derivative was obtained by distillation in steam as an almost colourless oil, solidifying on cooling to 0° . Two crystallisations from alcohol at temperatures below 0° furnished a white, crystalline powder melting at $9-10^{\circ}$ (Found: Cl = 16.44. $C_{12}H_{15}OCl$ requires Cl = 16.83 per cent.). This substance had a characteristic odour similar to that of honey, but not so powerful as that of 4-chlorophenyl *n*-propyl ketone.

Oxidation with chromic acid solution gave an acid which crystallised from alcohol in small, white needles melting at 165° after one crystallisation. This acid is presumably *5-chloro-2:4-dimethylbenzoic acid*, which does not appear to have been previously described.

2:6-Dinitro-m-4-xylyl n-Propyl Ketone (XX).—*m*-4-Xylyl *n*-propyl ketone (1 gram) was nitrated by adding its solution in 9 grams of concentrated sulphuric acid to a mixture of 10.5 grams of nitric acid (*d* 1.5; free from nitrous acid) and 27 grams of sulphuric acid, cooled to -12° , and stirred continuously. On pouring on to ice, a milky, semi-solid mass separated, which was taken up with ether and washed successively with sodium carbonate solution, dilute sodium hydroxide, and water. Evaporation of the solvent gave *2:6-dinitro-m-4-xylyl n-propyl ketone* as a pale yellow oil which solidified after two or three weeks; it separated from alcohol in a mass of white, hair-like needles melting at 63° (Found: N = 10.78. $C_{12}H_{14}O_5N_2$ requires N = 10.52 per cent.).

IV. *p*-Dibutylbenzene (XXII).

p-Di-*n*-butylbenzene was prepared by the action of sodium on a mixture of *p*-dichlorobenzene and *n*-butyl chloride. The yield, however, was small, and the numerous by-products obtained added to the difficulty of isolating the hydrocarbon in a pure state.

The reaction was carried out in a capacious flask immersed in an oil-bath, heated to 110° and subsequently to 150° . *n*-Butyl chloride (72 grams) and *p*-dichlorobenzene (60 grams) dissolved in 50 c.c. of xylene were gradually added to 50 grams of sodium shavings covered with xylene (75 c.c.), so that the heat of the reaction was just sufficient to keep the solvent boiling. The product was filtered to remove sodium and sodium chloride, and the cake of mineral matter was extracted thoroughly with warm benzene. After the bulk of the solvent had been removed from the combined extract

and washings, a dark brown, viscous residue remained, having a faintly green appearance in reflected light. The product was distilled, fractions being collected up to 280—300°. By means of a lengthy process of fractionation, followed by treatment with metallic sodium, *p-di-n-butylbenzene* was obtained boiling at 224—225.5°/759 mm. (Found : C = 88.75, 88.76; H = 10.95, 11.30. $C_{14}H_{22}$ requires C = 88.34; H = 11.66 per cent.). After further distillations, the hydrocarbon gave C = 88.65; H = 11.3 per cent. Appreciable quantities of diphenyl were obtained in the reaction, and no doubt the presence of traces of diphenyl accounts for the high carbon content of the hydrocarbon. *p-Di-n-butylbenzene* is a colourless liquid having a faint, agreeable, orange-like odour.

2-Nitro-1 : 4-di-n-butylbenzene.—Dibutylbenzene (7 grams) was cooled to 0° and fuming nitric acid added in small quantities until 20 grams had been used. At the commencement of the operation the acid layer became dark red. The hydrocarbon on the other hand darkened as the nitration proceeded, until it was almost indistinguishable from the lower stratum. The nitration was checked as soon as nitrous fumes were evolved and the upper layer became lighter in colour. The crude nitro-compound was separated and treated repeatedly with water and sodium hydroxide solution until the washings were not tinted red. It was purified by distillation in steam, when *2-nitro-1 : 4-di-n-butylbenzene* was obtained as a pale yellow, refractive liquid, having a pleasant and characteristic odour, faintly resembling that of lemons. It was purified for analysis by further distillation in steam, the first and the last portions of the distillate being rejected (Found : N = 6.14. $C_{14}H_{21}O_2N$ requires N = 5.95 per cent.).

2-Amino-1 : 4-di-n-butylbenzene (XXIII).—The reduction of *2-nitro-1 : 4-dibutylbenzene* to the corresponding amino-compound did not proceed smoothly when zinc dust and ammonium chloride, or tin or zinc with aqueous or alcoholic hydrochloric acid were employed as reducing agents. More favourable results were obtained by the use of iron filings and acetic acid, but even under these conditions the product was contaminated with appreciable quantities of a less basic substance.

The nitro-compound (6.4 grams), dissolved in 15 c.c. of glacial acetic acid, was gradually added to 15 grams of iron filings covered with 50 grams of 80 per cent. acetic acid. The mixture was gently heated during the addition of the nitrodibutylbenzene and for a period of one hour after all the nitro-compound had been added. The bulk of the acetic acid was removed by distillation, and the crude amine isolated by distillation in steam after making the residue

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alkaline. It was partly purified by conversion into the sparingly soluble *sulphate*, which was extracted with ether. From the sulphate a moderately pure specimen of the base was obtained as a colourless liquid having a faint yet characteristic odour somewhat resembling that of mushrooms. The *hydrochloride*, which is soluble in water or chloroform, separated from dilute hydrochloric acid in white, flattened needles.

2-Benzoylamino-1 : 4-di-n-butylbenzene, after repeated crystallisation from alcohol, separated in white masses of needles melting at 116° (Found : C = 81.4; H = 8.6. $C_{21}H_{27}ON$ requires C = 81.5; H = 8.8 per cent.).

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