Reactions of Diazonium Salts with Phenols and Amines in Non-Aqueous Media

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Although diazonium salts have been known for more than a century only a few have been described which are soluble in benzene or ether and this has limited the study of their reactions.[1] In some investigations suspensions of diazonium salts or their complexes with zinc chloride have been used, but it was hoped to obtain simpler results in the present study from experiments in homogeneous solution.

Diazonium salts which are soluble in benzene are readily prepared by applying normal methods of diazotisation to alkoxyanilines having *n*-heptyl, *n*-decyl or cetyl groups in the alkoxy substituents. *p*-*n*-Decyloxybenzenediazonium fluoborate and the corresponding *perchlorate,* for example, are both soluble in cold benzene. The diazonium salts of this type are colourless to pale yellow crystalline compounds of low melting-point, most of which are stable when kept for long periods in the dry state. The solubility in benzene depends on the anion and whilst *p*-*n*-decyloxybenzenediazonium fluoborate forms a 4% solution in benzene at the room temperature the *chloride* and *toluene*-p-*sulphonate* are less soluble and the sulphate almost insoluble. The character of the *chloride* as a true diazonium salt is established by the following considerations. It reacts immediately and quantitatively with silver perchlorate in benzene forming silver chloride, and combines with stannic chloride to form the derivative $(C_{10}H_{21}OC_6H_4N_2)_2SnCl_6$. With iodine monochloride it forms $(C_{10}H_{21}OC_6H_4N_2)^+ICl_2^-$. The diazonium character of the perchlorates and fluoborates is ensured by the nature of their anions.

On the addition of a benzene solution of tetra-*n*-butylammonium hydroxide to one of *p*-*n*-decyloxybenzenediazonium fluoborate an orange colour develops immediately and increases in intensity until two mols of the base have been added. This corresponds to the formation of the tetra-*n*-butylammonium salt of the diazotate:

$$\begin{gathered}(p\text{-}n\text{-}C_{10}H_{21}OC_6H_4N_2)^+BF_4^- + 2\,(Bu_4N)^+OH^- \\ \downarrow \\ (p\text{-}n\text{-}C_{10}H_{21}OC_6H_4\text{—}N\text{=}N\text{—}O)^-NBu_4^+ + \\ + (Bu_4N)^+BF_4^- + H_2O\end{gathered}$$

or of the related *iso*diazotate. The latter is the more probable because it does not couple to β-naphthol, nor to dimethylaniline, even after the addition of glacial acetic acid equivalent in amount to the base.

The reaction with sodium iodide follows a different course. On the addition of sodium iodide in dry acetone to a benzene solution of *p*-*n*-decyloxybenzenediazonium fluoborate *p*-*n*-decyloxyiodobenzene is formed together with iodine and *p*-*n*-decyloxydiphenyl, the two last mentioned products being present in equivalent amount. The proportion of these relative to *p*-*n*-decyloxyiodobenzene increases with dilution and this suggests the following course of events in which radical reactions play an important part:

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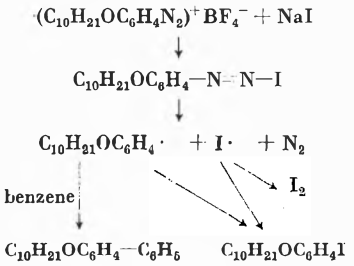
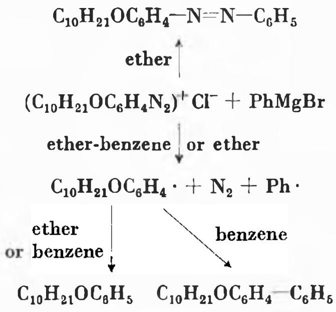
[1] W. BRADLEY and J. D. THOMPSON, *Nature 178* (1956) 1069.

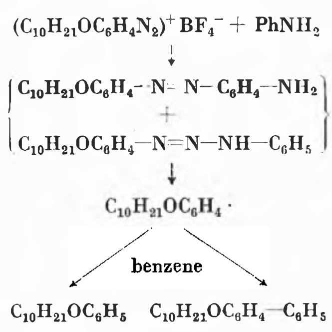


The product also contained a very small proportion of diphenyl which must have arisen through the intermediate formation of phenyl radicals.[2]

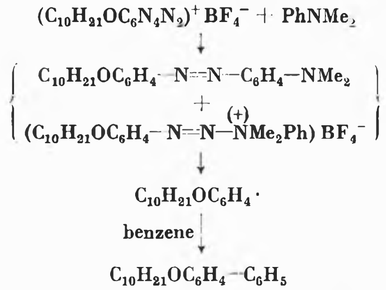
Addition of phenylmagnesium bromide prepared in ether to a benzene solution of *p-n*-decyloxybenzenediazonium chloride readily gave nitrogen but the expected *p-n*-decyloxyazobenzene was formed only in minute yield. The main products were *n*-decyloxybenzene, *p-n*-decyloxydiphenyl, and diphenyl. Evidently with Grignard reagents in benzene, although ionic reactions occur which result in the formation of unsymmetrical azo compounds, diazonium salts react mainly through radicals. When the reaction was carried out wholly in ether *p-n*-decyloxydiphenyl was no longer obtained but the yield of *n*-decyloxybenzene was greatly enhanced. In this medium the yields of azo compounds were higher. The following scheme summarises the observations:



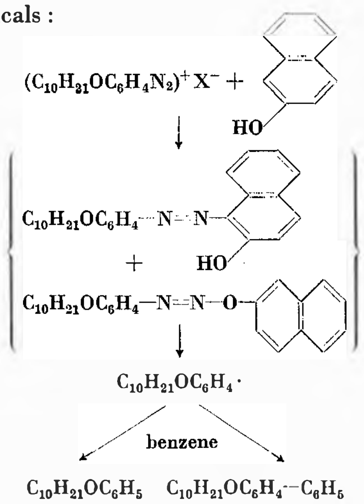
With aniline (2 mol) in benzene at 15° *p-n*-decyloxybenzenediazonium salts react to form *p-n*-decyloxydiazoamino-benzene and 4-amino-4′-*n*-decyloxyazobenzene. The diazoaminobenzene derivative is unstable and readily decomposes forming *n*-decyloxyphenyl radicals which react with the solvent to form *n*-decyloxybenzene and *p-n*-decyloxydiphenyl. The following scheme represents the course of the reaction:



An analogous reaction occurs with dimethylaniline. In addition to the expected product of the reaction, 4-dimethylamino-4′-*n*-decyloxyazobenzene, there was formed also *p-n*-decyloxydiphenyl. This implies the intermediate formation of *n*-decyloxyphenyl radicals in such a scheme of reactions as:



The tendency for radical reactions to occur when benzene is used as the medium was shown also in the reaction of *p-n*-decyloxybenzenediazonium salts with the dry sodium salt of β-naphthol. In this example too, although 1-*p-n*-decyloxyphenylazo-2-naphthol is formed as the main product, there is produced also *p-n*-decyloxydiphenyl. The origin of this derivative is probably to be attributed to the intermediate formation of a diazo-ether which decomposes yielding *n*-decyloxyphenyl radicals:



No reaction occurs when free β-naphthol is added to a solution of *p-n*-decyloxybenzenediazonium fluoborate in benzene, but the expected azo compound is formed when pyridine or tetra-*n*-butylammonium hydroxide is present. The reaction in the presence of pyridine was investigated in greater detail.

In the first experiments the concentrations of the diazonium salt and β-naphthol were approximately the same (4×10^{-4} g mol); pyridine (6.38×10^{-4} g mol) was present also, and the combined volume of reactants and medium was 50 ml at 20 ± 0.2 °C. Formation of the azo compound occurred, and at suitable intervals 2 ml portions of the solution were withdrawn and mixed with 25 ml of glacial acetic acid. A further quantity of the acid was then added to bring the total volume to 50 ml. The optical density of the solution was measured at

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[2] *idem.*, *ibid.* *186* (1960) 631.

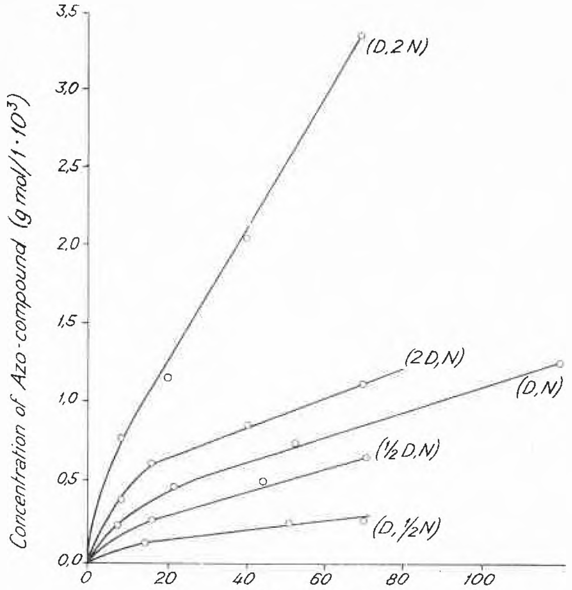


Fig. 1. The Rate of Coupling of *p-n*-Decyloxybenzenediazonium Fluoborate with β-Naphthol in Benzene (Pyridine)

466 mμ and the concentration of azo-compound present was obtained by comparison with a previously determined graph relating the optical density at 466 mμ of solutions of known concentrations of pure 1-*p*-*n*-decyloxyphenylazo-2-naphthol in a medium consisting of benzene (4 vol) and glacial acetic acid (96 vol). Over the concentration range studied (0 to 1.2 mg of azo-compound in 50 ml of solution) the graph was a straight line. The results are shown in the Tables 5 to 9 (Experimental) and graphically in Figure 1. It is clear from the curves that there is initially a brief, relatively rapid formation of azo-compound occurring during about 20 minutes, after which a much slower reaction takes place at an almost constant rate, though falling slowly with time. The overall rate of reaction may be gauged from the fact that after 2 hours the yield of azo-compound is approximately 16.5% of the theoretical, and 66% after 50 hours.

In subsequent experiments the initial concentration of the diazonium salt was varied and it was found that the amount of azo-compound formed at a given time was roughly proportional to the square root of the initial diazonium salt concentration.

Thus at $t = 70$ min the concentration of azo-derivative with different initial amounts of diazonium salt (β-naphthol and pyridine concentration fixed) was:

Table 1

Concentration of Azo-compound (g mol/l × 10³) = (a)	Relative Concentration of Diazonium Salt = (b)	$(b)^{-1/2}$ = (c)	$\frac{(c)}{(a)}$
0.625	0.5	0.707	1.13
0.875	1.0	1.000	1.14
1.125	2.0	1.416	1.26

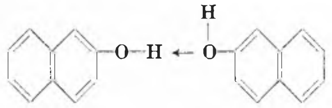
This implies that the diazonium salt is present mainly as a dimer, and that dissociation to a monomolecular form occurs, the monomer reacting as fast as it is formed. The view that an active monomeric form is being produced from a dimer would explain the observed initial rapid rate of coupling, because the diazonium salt solution when first prepared would be expected to contain the monomer at a higher concentration than at any subsequent time.

When the initial concentrations of the diazonium salt and pyridine were fixed and that of the β-naphthol was varied, it was found that the amount of azo-compound produced after a given time was approximately proportional to the square of the initial naphthol concentration. Thus at $t = 70$ min the concentration of azo-compound was related to the initial naphthol concentration as shown in the following table.

Table 2

Relative Initial Concentration of β-naphthol = (b)	Concentration of Azo-compound (g mol/l × 10³) = (a)	$(b)^{1.75}$ = (c)	$\frac{(c)}{(a)}$
10	0.30	56.2	187
20	0.875	189	216
40	3.40	635	186

At $t = 60$ min the corresponding values of $\frac{(c)}{(a)}$ are 204, 236 and 212. Evidently two molecules of β-naphthol are involved in the formation of one molecule of azo compound. This situation would arise if β-naphthol reacted relatively slowly with itself to form a dimer which then coupled with the diazonium salt, the coupling rate being faster than the dimerisation. One possible form of the dimer would be



and in this it is possible that the nucleus on the left would couple more readily than that of single molecules of β-naphthol. Another possibility is that the diazonium fluoborate and β-naphthol react to form the ion-pair

$$(p\text{-}n\text{-}C_{10}H_{21}OC_6H_4-\overset{\oplus}{N}\equiv N)\,(\overset{\ominus}{O}-C_{10}H_7)$$

which then reacts further with another molecule of β-naphthol, possibly by a mechanism analogous to that suggested by **Ingold**[3] to explain the rearrangement of diazoamino into aminoazo compounds.

The effect of pyridine is smaller than that of tetra-*n*-butylammonium hydroxide and no evidence could be obtained that pyridine perceptibly increased the ionisation of β-naphthol at the concentrations employed. It is possible that its accelerating effect is due to the formation of a pyridine-β-naphthol adduct:

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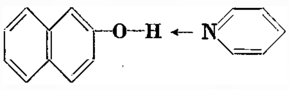
[3] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, p. 612.



In addition pyridine tends to reverse the association of long-chain compounds.

In the presence of tetra-*n*-butylammonium hydroxide the coupling reaction was very fast indeed. Using the β-naphthol and *p*-*n*-decyloxybenzenediazonium fluoborate at concentrations of about 8×10^{-3} g mol/litre the coupling was complete within one minute, the amount of dye formed being proportional to the amount of the tetra-*n*-butylammonium hydroxide added until one equivalent of the base had been reached. This result could have arisen either because the base ionizes the β-naphthol or because the base reacts with the diazonium salt to form a more reactive derivative. These points were settled by the following considerations.

The importance of the ionisation of β-naphthol was shown in a series of experiments in which increasing amounts of tetra-*n*-butylammonium hydroxide were added to the β-naphthol before the diazonium salt was introduced. In each experiment coupling occurred very rapidly indeed, it was almost complete within one minute, and the amount of azo-compound formed was nearly proportional to the amount of base added up to one equivalent.

A very different effect was observed if the base was added to the diazonium salt first, the β-naphthol being added last. No coupling occurred under these conditions because the diazonium salt reacted very rapidly with the base to form a non-coupling, inactive *iso*diazotate. The same kind of reaction is already well known in aqueous solutions but what is remarkable about the reaction in benzene is the great ease with which it occurs. In aqueous solution it is usually necessary to employ an excess of concentrated alkali to produce the inactive *iso*diazotates, and it seems that the medium may play an important role in facilitating the second stage of the following reaction sequence:

$$\text{diazonium ion} \xrightarrow{\text{OH}'} \text{diazotate ion} \longrightarrow \textit{iso}\text{diazotate ion.}$$

The origin of this may be the same as for the reaction reported by PATTERSON and MONTGOMERIE[4] who found that at 26° the rate of isomerisation of *syn*-anisaldoxime into the *anti*-form was about 50% faster in benzene than in methanol or ethanol (relative k_{26°: MeOH 2.07, EtOH 1.86, C_6H_6 3.13%).

It may be mentioned that not only does the *iso*diazotate fail to react with β-naphthol, it does not react either with dimethylaniline even after the addition of glacial acetic acid equivalent in amount to the base present.

These results have an important bearing on the results which are obtained when the diazonium salt and the β-naphthol are mixed first and then the base added later. Experiment shows that a high yield of azo-compound results, which indicates that the reaction of the base with β-naphthol is even faster than its reaction with the diazonium salt.

Following are the general points of interest which have emerged from a study of the chemistry of diazonium salts and the coupling reaction in benzene.

Diazonium salts containing higher alkoxy groups as substituents are soluble in benzene, fluoborates and perchlorates being more soluble than chlorides and toluene-*p*-sulphonates. Solutions of the chlorides show ion-exchange reactions with silver perchlorate and combine with stannic chloride and iodine monochloride like typical diazonium salts. Solutions of all the salts are stable at the room temperature. Addition of sodium iodide causes decomposition with formation of nitrogen, free iodine, alkoxyiodobenzenes and alkoxydiphenyls as the result of radical reactions. The first three products are obtained also when diazonium salts react with sodium iodide in water, but the formation of diphenyl and alkoxydiphenyls emphasises the radical character of the reaction in benzene. Analogous products are obtained when Grignard reagents are used. Here again the reaction is essentially radical in character though a ionic reaction occurs in small degree.

With aniline diazo-amino- and amino-azo-compounds are formed, as in aqueous solution, but the diazo-amino-compounds proved to be unstable, decomposing with formation of nitrogen, alkoxybenzenes and diphenyl. The formation of the last in particular emphasises the radical character of the reaction. Analogous results were obtained using dimethylaniline.

The main conclusion from these experiments is that diazonium salts in benzene react primarily by ionic reactions, but these are frequently succeeded by radical reactions due to the decomposition of diazoiodides, diazoethers and diazo amino-compounds formed during the first stage of the total reaction.

These results are of interest for the further consideration of the coupling reaction in benzene.

In the absence of other reagents diazonium salts couple slowly with dimethylaniline and do not couple with β-naphthol. This is normal experience in aqueous solution, in which dimethylaniline is weakly reactive and β-naphthol inactive towards typical diazonium salts.

When an excess of tetra-*n*-butylammonium hydroxide is added to a benzene solution of *p*-*n*-decyloxybenzenediazonium fluoborate the diazonium salt reacts at once to form the corresponding *iso*-diazotate. This does not couple to either β-naphthol or dimethylaniline. In benzene, as in water therefore, it is the diazonium salt which is the reactive component.

On the other hand tetra-*n*-butylammonium hydroxide ionises the β-naphthol which then reacts immediately with the diazonium salt, the yield of azo-compound formed from equivalent quantities of diazonium salt and

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[4] T. S. PATTERSON and H. H. MONTGOMERIE, *J. Chem. Soc. 101* (1912) 26.

naphthol being proportional to the amount of the hydroxide added, over the range 0.1 to 1.0 equivalents. These experiments show clearly how little is the coupling reaction affected in mechanism or speed by changing the medium from water to benzene.

The coupling reaction in benzene in the presence of pyridine follows a more complicated course. Addition of pyridine enables the reaction to proceed but the rate is much slower than with tetra-*n*-butylammonium hydroxide. Pyridine has no apparent effect on the diazonium salt, nor does it have any appreciable influence on the light absorption spectrum of β-naphthol in benzene. However, with the enormous effect of tetra-*n*-butylammonium hydroxide in mind it does seem possible that the whole of the effect of pyridine could be due to an increase in the reactivity of β-naphthol following association with the base.

In the pyridine-catalysed reaction the rate depends on the square root of the initial diazonium salt concentration, which suggests that the salt exists mainly as a dimer in benzene, the active monomeric form being produced from it at a low rate. The rate of dissociation of the dimeric form is not important in the tetra-*n*-butylammonium hydroxide catalysed reaction for the reason that the anion of β-naphthol is reactive enough to decompose the dimer.

A final point of interest is that β-naphthol and 1-D-2-naphthol couple at identically the same rate with *p*-*n*-decyloxybenzenediazonium fluoborate in benzene in the presence of pyridine. There is no kinetic isotope effect, such as ZOLLINGER[5] found. Reference must be made also to the work of HUISGEN[6] who observed that diazoacetates coupled with β-naphthol in benzene containing acetic acid.

The main conclusion from the work as a whole is that the coupling reaction in benzene ist not essentially different from that which occurs in aqueous solution, but that by-products may arise from radical reactions if the conditions of coupling favour the formation of diazoethers or diazoamino compounds at the first stage of the total reaction.

Experimental

*1,4-Di-*n*-decyloxy-2-nitrobenzene.* A suspension of *p*-di-*n*-decyloxybenzene (27.0 g) in glacial acetic acid (700 cm³) was stirred at the room temperature whilst a solution of nitric acid (12.6 cm³, *d* 1.42) in glacial acetic acid (140 cm³) was added, heated slowly to 40°, and kept at this temperature for 20 min. The clear yellow solution was added to water (750 cm³), the precipitate which was formed was extracted with benzene (3 × 300 cm³), and the extracts were washed with 10% sodium hydroxide, then water. Evaporation of the solvent and distillation of the residue gave a pale yellow oil (29 g, b. p. 212 to 216°/0.05 mm.

Found: C 71.8, H 10.2, N 3.3%; $C_{26}H_{45}NO_4$ requires: C 71.7, H 10.4, N 3.2%.

On being heated for 20 h with hydrated sodium sulphide (50 g) in water (32 cm³) the nitro-derivative (17.0 g) in alcohol (100 cm³) gave 2,5-di-*n*-decyloxyaniline (11.5 g).

*1,2-Di-*n*-decyloxy-4-nitrobenzene.* A solution of nitric acid (9.0 cm³, *d* 1.42) in glacial acetic acid (100 cm³) was added at 24° over 15 min to a suspension of *o*-di-*n*-decyloxybenzene (19.0 g) in glacial acetic acid (100 cm³) and then the temperature was raised to 55°. The suspension which was formed was cooled, water (300 cm³) was added and the 1,2-di-*n*-decyloxy-4-nitrobenzene (20.5 g) so obtained was crystallised from alcohol in pale yellow needles, m.p. 67–69°

Found: C 71.6, H 10.1, N 3.0%; $C_{26}H_{45}NO_4$ requires: C 71.7, H 10.4, N 3.2%.

On being refluxed for 12 h with hydrated sodium sulphide (80 g) in water (50 cm³) the nitro-compound (21.75 g) in alcohol (200 cm³) gave 14 g of 3,4-di-*n*-decyloxyaniline.

*2,6-Dichloro-4-*n*-decyloxyacetanilide.* On being stirred with glacial acetic acid (100 cm³) and acetic anhydride (28 cm³), 4-amino-3,5-dichlorophenol (48.5 g) gave 45.1 g of 2,6-dichloro-4-hydroxyacetanilide which was crystallised from aqueous methanol as felted needles, m.p. 217°.

Found: C 43.8, H 3.1, N 6.1%; $C_8H_7NO_2Cl_2$ requires: C 43.6, H 3.2, N 6.4%.

2,6-Dichloro-4-hydroxyacetanilide (22 g) refluxed for 6 h in ethanol (200 cm³) with *n*-decyl bromide (24.3 g) and sodium hydroxide (5.0 g) in water (10 cm³) gave 23.8 g of 2,6-dichloro-4-*n*- decyloxyacetanilide, crystallised from methanol as needles, m.p. 111–112°.

Found: C 60.1, H 7.5, N 3.7%; $C_{18}H_{27}NO_2Cl_2$ requires: C 60.0, H 7.5, N 3.9%.

On being refluxed for 4 h with a mixture of 10% hydrochloric acid (60 cm³) and ethanol (75 cm³) this derivative gave 2,6-dichloro-4-*n*-decyloxyaniline hydrochloride (19.8 g).

*p-*n*-Decylsulphonylacetanilide.* Prepared (80 g) by 6 h refluxing of *p*-acetamidobenzenesulphinic acid (80 g) in ethanol (600 cm³) with *n*-decyl bromide (88.5 g) and sodium hydroxide (17.6 g) in water (30 cm³). Crystallisation from benzene-light petroleum (b. p. 60 to 80°) gave *p*-*n*-decylsulphonylacetanilide as colourless needles, m.p. 99 to 100°.

Found: N 4.1, S 9.3%; $C_{18}H_{29}NO_3S$ requires: N 4.1, S 9.4%.

This derivative (68 g) on being refluxed with concentrated hydrochloric acid (200 cm³) and ethanol (400 cm³) for 3 h gave 54 g of *p*-*n*-decylsulphonylaniline.

Other amines were prepared by alkylation of *p*-hydroxyacetanilide followed by hydrolysis. Analyses and m. pts. are shown in Table 3. Figures in parenthesis indicate softening temperatures. An asterisk means soluble in benzene.

*p-*n*-Decyloxybenzenediazonium toluene-p-sulphonate.* Prepared (44 g) by diazotizing *p*-*n*-decyloxyaniline hydrochloride (29.4 g) in water (750 cm³) with sodium nitrite (7.3 g) in water (25 cm³) at 20°, and the addition of toluene-*p*-sulphonic acid monohydrate (30 g) in water (90 cm³). The pale yellow oil which separated gradually solidified. Crystallisation from benzene at 60° gave colourless needles, m.p. 114° (decomp.),

Found: C 63.8, H 7.6, N 6.5, S 7.6%; $C_{23}H_{32}N_2O_4S$ requires: C 63.9, H 7.4, N 6.5, S 7.4%.

The *chloride* formed colourless blades (decomp. 92°); it could not be analysed satisfactorily because hygroscopic. The *fluoborate* (33.0 g) prepared by the addition of sodium fluoborate (11.6 g) in water (100 cm³) to a solution of the diazonium chloride obtained from *p*-*n*-decyloxyaniline hydrochloride (28.6 g) was crystallised from ethanol as colourless needles which softened at 88° and decomposed at 108°.

Found: C 55.4, H 7.6, N 8.2%; $C_{16}H_{25}N_2OBF_4$ requires: C 55.2, H 7.2, N 8.1%.

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[5] H. ZOLLINGER, *Helv. Chim. Acta 38* (1955) 1597.

[6] R. HUISGEN, *Liebigs Ann. Chem.* 574 (1951) 184.

Table 3

Substituent	Derivative	m.p. (°C)	Found					Compound	Required				
			C	H	N	S	Cl		C	H	N	S	Cl
p-*n*-Butoxy	HBr*	170	–	–	5.7	–	–	$C_{10}H_{16}NOBr$	–	–	5.6	–	–
	β-$C_{10}H_7SO_3H$	222	–	–	3.7	–	–	$C_{20}H_{27}NO_4S$	–	–	3.8	–	–
p-*n*-Heptyloxy	HCl*	242 (105)	–	–	5.9	–	–	$C_{13}H_{22}NOCl$	–	–	5.8	–	–
	p-$C_7H_7SO_3H$	140 (122)	–	–	3.9	–	–	$C_{20}H_{29}NO_4S$	–	–	3.7	–	–
	N-acetyl	90–91	–	–	5.6	–	–	$C_{15}H_{23}NO_2$	–	–	5.6	–	–
p-*n*-Decyloxy	HCl*	242 (108)	–	–	4.9	–	–	$C_{16}H_{28}NOCl$	–	–	4.9	–	–
	p-$C_7H_7SO_3H$*	127	–	–	3.3	–	–	$C_{23}H_{35}NO_4S$	–	–	3.5	–	–
	N-acetyl	92	–	–	5.1	–	–	$C_{18}H_{29}NO_2$	–	–	4.8	–	–
p-Cetyloxy	*p*-$C_7H_7SO_3H$*	164 (126)	–	–	2.7	–	–	$C_{29}H_{47}NO_4S$	–	–	2.8	–	–
	N-acetyl	96–97	–	–	3.7	–	–	$C_{24}H_{41}NO_2$	–	–	3.7	–	–
p-Benzyloxy	*p*-$C_7H_7SO_3H$	186	–	–	4.3	–	–	$C_{20}H_{21}NO_4S$	–	–	3.8	–	–
o-Decyloxy	*p*-$C_7H_7SO_3H$*	91–92	65.1	8.2	3.4	7.7	–	$C_{23}H_{35}NO_4S$	65.6	8.3	3.3	7.6	–
	N-acetyl	55–56	–	–	4.9	–	–	$C_{18}H_{29}NO_2$	–	–	4.8	–	–
3-Allyl-4-*n*-decyloxy	HCl*	89–91	70.1	9.6	4.7	–	11.0	$C_{19}H_{32}NOCl$	70.0	9.8	4.3	–	10.9
	N-acetyl	104–106	76.2	9.9	4.3	–	–	$C_{21}H_{33}NO_2$	76.1	10.0	4.2	–	–
2,5-Di-*n*-decyloxy	base	42–44	77.2	11.8	3.6	–	–	$C_{26}H_{47}NO_2$	77.0	11.6	3.5	–	–
	HCl*	116–118	–	–	3.5	–	8.0	$C_{26}H_{48}NO_2Cl$	–	–	3.2	–	8.1
	p-$C_7H_7SO_3H$*	133–134	69.1	9.6	2.3	5.4	–	$C_{35}H_{55}NO_5S$	68.7	9.5	2.4	5.6	–
	N-acetyl	64–66	75.0	10.8	3.2	–	–	$C_{28}H_{49}NO_3$	75.2	11.0	3.1	–	–
3,4-Di-*n*-decyloxy	base	44–45	77.2	11.7	3.6	–	–	$C_{26}H_{47}NO_2$	77.0	11.6	3.5	–	–
	p-$C_7H_7SO_3H$*	143–144	69.1	9.6	2.5	5.5	–	$C_{33}H_{55}NO_5S$	68.7	9.5	2.4	5.6	–
	N-acetyl	101	75.2	10.8	3.1	–	–	$C_{28}H_{49}NO_3$	75.2	11.0	3.1	–	–
2,6-Dichloro-4-*n*-decyloxy	HCl	192	–	–	3.9	–	–	$C_{16}H_{26}NOCl_3$	–	–	4.0	–	–
	N-acetyl	111–112	60.1	7.5	3.7	–	–	$C_{18}H_{27}NO_2Cl_2$	60.0	7.5	3.9	–	–
p-*n*-decyl sulphonyl	base	112	64.8	9.0	4.9	10.7	–	$C_{16}H_{27}NO_2S$	64.6	9.1	4.7	10.8	–
	HCl	221 (dec.)	58.0	8.5	4.2	9.8	11.1	$C_{16}H_{28}NO_2SCl$	57.6	8.4	4.2	9.6	10.6
	N-acetyl	99–100	–	–	4.1	9.3	–	$C_{18}H_{29}NO_3S$	–	–	4.1	9.4	–

Its solubility in benzene was approx. 4% at 21°. The *perchlorate* crystallised from ethanol as blades, m. p. 92° (decomp.).

Found: C 53.5, H 7.3, N 8.1, Cl 10.2%; $C_{16}H_{25}N_2O_5Cl$ requires: C 53.3, H 6.9, N 7.8, Cl 9.9%.

p-n-*Decyloxybenzenediazonium chloride-zinc chloride double salt* crystallised from acetone or ethanol as colourless blades or plates, m.p. 121° (decomp.).

Found: C 52.7, H 6.8, N 7.9%; $C_{32}H_{50}N_4O_2Cl_4Zn$ requires: C 52.7, H 6.9, N 7.7%.

All four salts were soluble in benzene.

Reactions in benzene

(1) A solution of silver perchlorate (0.736 g, dried at 110°) in dry benzene (15 cm³) at 40° was added with stirring to one of *p*-*n*-decyloxybenzenediazonium chloride (1.057 g) in benzene (15 cm³) at 63°. After 2 h the precipitate of silver chloride was collected, washed with benzene, and dried (0.503 g, calc. 0.5105 g). Addition of the benzene mother liquors and washings to a solution of β-naphthol (0.6 g) in benzene (20 cm³) containing pyridine (0.5 cm³) gave pyridine perchlorate, m.p. 286° (0.61 g, calc. 0.64 g) and 1-*p*-*n*-decyloxyphenylazo-2-naphthol (1.22 g, calc. 1.24 g), m.p. 76 to 77°, after crystallisation from ethanol.

(2) A solution of stannic chloride (0.26 g) in dry benzene (10 cm³) added to a suspension of *p*-*n*-decyloxybenzenediazonium chloride (0.59 g) in the same solvent (20 cm³) gave bis (p-n-*decyloxybenzenediazoniumhexachlorostannate* (0.25 g) which was crystallised as white needles, decomp. 126°.

Found: C 44.9, H 5.7, N 6.6, Cl 25.1%; $C_{32}H_{50}N_4O_2Cl_6Sn$ requires: C 45.0, H 5.9, N 6.6, Cl 25.0%.

(3) Iodine trichloride (1.3 g) in dry benzene (10 cm³) at 5° was stirred into a suspension of *p*-*n*-decyloxybenzenediazonium chloride (1.5 g) in the same medium (25 cm³) at 20°. A voluminous yellow precipitate was formed. This dissolved on being heated to 50° and on being cooled the solution gave p-n-*decyloxybenzenediazonium dichloroiodide* (2.3 g, yield, 99%) which was crystallised from benzene as pale yellow plates, m.p. 118° (decomp.).

Found: C 42.1, H 5.4, N 6.1%; $C_{16}H_{25}N_2OICl_2$ requires: C 41.8, H 5.5, N 6.1%.

9.525 mg of this derivative gave 10.81 mg (required 10.80 mg) of mixed silver halides.

The same derivative (0.3 g) was formed by the reaction of iodine monochloride (0.12 g) with *p*-*n*-decyloxybenzenediazonium chloride (0.2 g) in benzene (10 cm³).

(4) a) A solution of aniline (2.32 g) in benzene (25 cm³) was stirred for 1 h with one of *p*-*n*-decyloxybenzenediazonium toluene-*p*-sulphonate (10.8 g) in benzene (250 cm³) at 62°. Aniline toluene-*p*-sulphonate (3.2 g, m.p. 226 to 228° and 238° after crystallisation from aqueous ethanol) separated overnight. The suspension was filtered, the filtrate chromatographed on alumina, and the bands developed with benzene. The first 125 cm³ of eluate was evaporated and the residue so

obtained was crystallised from ethanol; *p*-*n*-decyloxydiphenyl (2.0 g) m.p. 76 to 78°, undepressed by the authentic derivative, was obtained. The mother liquor was evaporated and the residual oil distilled to give diphenyl (25 mg) as a white sublimate, m.p. 58 to 66°, *n*-decyloxybenzene (0.4 g) as a pale yellow oil, b.p. 90 to 140° (bath temp.)/0.01 m.m., and *p*-*n*-decyloxydiphenyl (0.15 g).

b) When the amount of aniline was 4.65 g and the reaction was at 20° for 30 h the products were aniline toluene-*p*-sulphonate (6.3 g, m.p. 234°), *p*-*n*-decyloxydiphenyl (1.15 g), diphenyl (0.12 g) and *p*-decyloxybenzene (0.42 g). After 750 cm^3 of eluate had been removed from the column the next 600 cm^3 was collected and evaporated. The solid (0.8 g) so obtained gave 4-amino-4′-decyloxyazobenzene (0.25 g), m.p. 100 to 102°, not depressed by the authentic derivative, after crystallisation from light petroleum (b.p. 40 to 60°).

c) Aniline (1.86 g) and *p*-*n*-decyloxybenzenediazonium toluene-*p*-sulphonate (4.32 g) stirred in benzene (25 cm^3) gave a precipitate of aniline toluene-*p*-sulphonate (2.4 g) and a mother liquor which was chromatographed on alumina. Several bands were formed and from these were obtained diphenyl (a trace), *n*-decyloxybenzene (50 mg) and *p*-*n*-decyloxydiphenyl (150 mg). The fourth band on being eluted with benzene (1350 cm^3) gave a solution which afforded a brown oil (1.6 g) on evaporation. Crystallisation of this from ethanol gave *p*-*n*-decyloxydiazoaminobenzene (1.1 g). The third band eluted with a mixture of benzene and acetone (600 cm^3 of 10:1) gave a brown oil which was crystallised from ethanol. A solid (0.22 g), m. p. 106 to 130°, separated and a mother liquor was obtained. From this evaporation to dryness and crystallisation from light petroleum (b. p. 40 to 60°) gave 4-amino-4′-decyloxyazobenzene (0.12 g), m.p. 99 to 101°, not depressed by the authentic derivative, after further crystallisation. The material, m.p. 106 to 130°, on being crystallised from ethanol and light petroleum (b.p. 40 to 80°) gave brown needles, m.p. 118 to 119°.

Found: C 74.3, H 9.1, N 11.5%; $C_{38}H_{55}N_5O_2$ requires: C 74.4, H 9.0, N 11.4%.

(5) a) Dimethylaniline (2.4 g) and *p*-*n*-decyloxybenzenediazonium chloride (3.0 g) were stirred in dry benzene (60 cm^3) at 60° and then kept overnight. Excess of dilute aqueous sodium hydroxide was then added and the organic layer was separated, washed, concentrated to 30 cm^3 and then chromatographed on alumina. Several bands were formed and from these were obtained by elution and crystallisation *p*-*n*-decyloxydiphenyl (0.4 g), 4-dimethylamino-4′-*n*-decyloxyazobenzene (0.9 g) and a derivative which crystallised from ethanol as brownish-yellow needles (80 mg), m. p. 101 to 103° and gave a violet coloration with hydrochloric acid.

Found: C 75.3, H 9.0, N 11.2%; $C_{24}H_{35}N_3O$ requires: C 75.6, H 9.2, N 11.0%

b) Dimethylaniline (1.21 g) and *p*-*n*-decyloxybenzenediazonium toluene-*p*-sulphonate (2.16 g) were stirred in dry benzene (35 cm^3) at the room temperature for 5 days, by which time the mixture no longer gave a red coloration when shaken with an aqueous solution of R-salt. Dimethylaniline toluene-*p*-sulphonate had separated as a red oil and the dark mother liquor was decanted and chromatographed on alumina. The products obtained were *p*-*n*-decyloxydiphenyl (15 mg), 4-dimethylamino-4′-*n*-decyloxyazobenzene (1.45 g, m.p. 103°) and a derivative (6 mg), m.p. 84 to 100°, which gave a violet coloration with hydrochloric acid.

(6) a) A solution of sodium iodide (3.832 g, 1 mol) in acetone (25 cm^3) was added dropwise with stirring to a solution of *p*-*n*-decyloxybenzenediazonium fluoborate (7.050 g, 1 mol) in dry benzene (200 cm^3) at 21°. Each drop produced a yellow coloration and a brisk evolution of gas; a precipitate of sodium fluoborate was formed. After 1 h the amount of free iodine, (0.152 mol) was determined in the supernatant brown solution by titration with standard sodium thiosulphate. The whole of the reaction product was then extracted with sodium thiosulphate solution, then the benzene solution was washed with water, dried and evaporated. The residual dark brown solid (6.2 g) was taken up in benzene (10 cm^3) and chromatographed on alumina. Three bands were formed and from these were obtained diphenyl (a trace), *p*-*n*-decyloxyiodobenzene, m.p. 21 to 22.5° (4.3 g, 0.6 mol) and *p*-*n*-decyloxydiphenyl, m.p. 74 to 78° (0.845 g, 0.137 mol), which after further crystallisation did not depress the m.p. of the authentic derivatives.

b) When the volume of benzene used was 600 cm^3 the products of the reaction were iodine (0.258 mol), diphenyl (0.0005 g), *p*-*n*-decyloxyiodobenzene (3.3 g, 0.46 mol) and *p*-*n*-decyloxydiphenyl (1.63 g, 0.263 mol).

Reaction of Diazonium Salts with β-Naphthol in Benzene

a) β-Naphthol (2.88 g, 1 mol) in dry ether (40 cm^3) was converted into the sodium salt by reaction with sodium (0.7 g) under nitrogen. After the addition of dry benzene (25 cm^3) the whole was added to one of *p*-*n*-decyloxybenzenediazonium toluene-*p*-sulphonate (8.64 g, 1 mol) in dry benzene (200 cm^3) at 60°. A red colour developed and this changed through orange to dark reddish-brown. Gas was evolved, sodium toluene-*p*-sulphonate was precipitated and after having been kept overnight was removed by filtration as a white powder (3.3 g, 0.87 mol). The filtrate was concentrated to 50 cm^3 and then chromatographed on alumina. Four main bands formed and from these were obtained *n*-decyloxybenzene (0.3 g, 0.065 mol), *p*-*n*-decyloxydiphenyl (0.4 g, 0.065 mol), and 1-(*p*-*n*-decyloxyphenylazo)-2-naphthol, m.p. 75 to 77° (5.75 g, 0.71 mol), raised to m.p. 78 to 79° by further crystallisation from ethanol.

Table 4

Substituent	m.p. (°C)	*Compound*	*Found*			*Required*		
			C	H	N	C	H	N
p-*n*-Propyloxy	121	$C_{19}H_{18}O_2N_2$	–	–	9.2	–	–	9.4
p-*n*-Butyloxy	106	$C_{20}H_{20}O_2N_2$	–	–	8.7	–	–	8.8
p-*n*-Heptyloxy	75–76	$C_{23}H_{26}O_2N_2$	–	–	8.0	–	–	7.7
p-sec.-Octyloxy	76–78	$C_{24}H_{28}O_2N_2$	76.3	7.4	7.4	76.6	7.5	7.5
p-*n*-Decyloxy	78–79	$C_{26}H_{32}O_2N_2$	–	–	7.1	–	–	6.9
p-Benzyloxy	141	$C_{23}H_{18}O_2N_2$	–	–	8.2	–	–	7.9
2,5-Di-*n*-decyloxy	103–104	$C_{36}H_{52}O_2N_2$	–	–	4.7	–	–	5.0
2,6-Dichloro-4-*n*-decyloxy	110–112	$C_{26}H_{30}O_2N_2Cl_2$	65.7	6.4	6.2	66.0	6.3	5.9
p-*n*-Decyl-sulphonyl	139–140	$C_{26}H_{32}O_3N_2S$	–	–	6.5	–	–	6.2

b) A solution containing *p-n*-decyloxybenzenediazonium perchlorate (0.7 g) in dry benzene (25 cm^3) at 24° was added to a stirred solution of β-naphthol (0.3 g) in benzene (25 cm^3) containing pyridine (0.5 cm^3); a red colour developed. After being kept overnight the precipitate of pyridine perchlorate, m. p. 288° (0.3 g, 88 % of calc.) was collected, the filtrate was concentrated and the residue which was obtained was crystallised from ethanol to give red prisms of 1-(*p-n*-decyloxyphenylazo)-2-naphthol (0.65 g, 85 % of calc.), m.p. 78 to 79°, not depressed by the authentic derivative.

In a similar preparation using *p-n*-decyloxybenzenediazonium toluene-*p*-sulphonate (4.3 g) in dry benzene (50 cm^3) at 60° and a solution of β-naphthol (1.5 g) in dry benzene (100 cm^3) containing pyridine (1.7 cm^3) at 55° the isolated products were pyridine toluene-*p*-sulphonate, m.p. 118 to 120° (2.0 g, 80 % of calc.) and 1-(*p-n*-decyloxyphenylazo)-2-naphthol, m.p. 73 to 76° (3.4 g, 85 % of calc.). The last was identical after crystallisation with the derivative prepared from diazotized *p-n*-decyloxyaniline hydrochloride (4.3 g) and β-naphthol (2.4 g) in aqueous alkaline solution; yield, 5.8 g, m.p. 78 to 79°.

Found: N 7.1 %; $C_{26}H_{32}N_2O_2$ requires: N 6.9 %.

The following derivatives of 1-phenylazo-2-naphthol were prepared by coupling diazonium salts to β-naphthol in sodium hydroxide-sodium carbonate solution; all were red in colour.

p-n-*Decyloxydiazoaminobenzene.* A solution of benzenediazonium chloride prepared from aniline (1.35 g) was added dropwise to a stirred suspension of *p-n*-decyloxyaniline (from 4.5 g of the hydrochloride) in ethanol (100 cm^3) and water (20 cm^3) containing anhydrous sodium acetate (8.2 g). The precipitate which was formed was collected, washed with water and crystallised (5 g) from aqueous ethanol as pale brown plates, m.p. 69 to 70°.

Found: C 74.4, H 8.7, N 11.6 %; $C_{22}H_{31}ON_3$ requires: C 74.8, H 8.8, N 8.9 %.

The *silver* derivative was crystallised from light petroleum (b.p. 40 to 60°) as a brown powder, m.p. 156° (decomp.).

Found: C 57.2, H 6.4 %; $C_{22}H_{30}ON_3Ag$ requires: C 57.4, H 6.5 %.

On being heated with aniline (1.7 g) and aniline hydrochloride (0.35 g) at 40° for 30 min and then at 50° for 8 h *p-n*-decyloxydiazoaminobenzene gave 4-*amino*-4′-*n*-*decyloxyazobenzene* (0.6 g) which was crystallised from benzene-light petroleum and then from methanol as brown needles, m.p. 102 to 103°.

Found: C 74.7, H 8.8, N 11.8 %; $C_{22}H_{31}ON_3$ requires: C 74.8, H 8.8, N 11.9 %.

4-*Acetamido*-4′-*n*-*decyloxyazobenzene* was crystallised from ethanol as pale yellow plates, m.p. 144°.

Found: C 73.0, H 8.6, N 10.5 %; $C_{24}H_{33}O_2N_3$ requires: C 72.9, H 8.4, N 10.6 %.

4-n-*Decyloxy*-4′-*dimethylaminoazobenzene.* Prepared (6.7 g) from dimethylaniline (2.42 g) and the diazonium salt from *p-n*-decyloxyaniline hydrochloride (5.7 g) in water (300 cm^3) containing ethanol (7.5 cm^3), concentrated hydrochloride acid (3.0 cm^3) and anhydrous sodium acetate (16.4 g). It was crystallised from ethanol as a yellow powder, m.p. 103°.

Found: N 11.3 %; $C_{24}H_{35}ON_3$ requires: N 11.0 %.

n-*Decyloxybenzene* prepared from phenol and decyl iodide had b.p. 103 to 104°/0.2 mm (Talvitie records b.p. 178°/15 mm).

Found: C 81.8, H 11.1 %, calc. for $C_{16}H_{26}O$: C 82.0, H 11.1 %.

p-n-*Heptyloxydiphenyl* was prepared by 4 h's heating of *p*-hydroxydiphenyl (4.25 g) and *n*-heptyl bromide (4.5 g) in ethanol (25 cm^3) with sodium hydroxide (1.1 g) in water (5 cm^3). It was crystallised from ethanol as white plates, m.p. 72 to 73°.

Found: C 84.9, H 9.2 %; $C_{19}H_{24}O$ requires: C 85.1, H 9.0 %.

p-n-*Decyloxydiphenyl* was prepared similarly using *n*-decylbromide (5.5 g). It was crystallised from ethanol as colourless plates, m.p. 78 to 79°.

Found: C 85.2, H 9.4 %; $C_{22}H_{30}O$ requires: C 85.2, H 9.7 %.

p-*Bromo*-n-*decyloxybenzene* prepared from *p*-bromophenol and *n*-decyl bromide was obtained as an oil, b.p. 124 to 126°/0.03 mm, which solidified to a colourless solid, m.p. 18°.

Found: C 61.2, H 8.1, Br 25.9 %; $C_{16}H_{25}OBr$ requires: C 61.4, H 8.0, Br 25.6 %.

p-n-*Decyloxyiodobenzene* prepared similarly from *p*-iodophenol was crystallised at 0° from methanol as colourless needles, m.p. 23.5°.

Found: C 53.3, H 6.9, I 35.2 %; $C_{16}H_{25}OI$ requires: C 53.3, H 6.9, I 35.3 %.

p-n-*Decyloxyazobenzene* prepared from *p*-hydroxyazobenzene crystallised from ethanol as yellow plates, m.p. 64 to 65°.

Found: C 77.8, H 9.0, N 8.7 %; $C_{22}H_{30}ON_2$ requires: C 78.1, H 8.9, N 8.3 %.

p-*Cetyloxyazobenzene,* prepared by GILES and NEUSTADTER, has m.p. 77 to 79°.

Found: C 79.7, H 10.1, N 6.3 %; calc. for $C_{28}H_{42}ON_2$: C 79.6, H 10.0, N 6.6 %

after crystallisation from light petroleum (b. p. 60 to 80°) and ethanol.

1-p-n-*Decyloxyphenylazonaphthalene* was prepared by 4 h's refluxing of 1-*p*-hydroxyphenylazonaphthalene (6.2 g) in ethanol (25 cm^3) with *n*-decyl bromide (5.5 g) and sodium hydroxide (1.1 g) in water (5 cm^3). It was crystallised from ethanol as yellow plates, m.p. 65 to 67°.

Found: C 80.3, H 8.4, N 7.1 %; $C_{26}H_{32}ON_2$ requires: C 80.4, H 8.3, N 7.2 %.

p-n-*Heptyloxybenzenediazonium fluoborate.* This derivative (1.35 g) was prepared from *p-n*-heptyloxyaniline hydrochloride (1.2 g) by the method used for the *p-n*-decyloxy analogue. It was obtained by crystallisation from ethanol at 3° in the form of needles, m.p. 70°.

Found: C 50.9, H 6.6, N 9.0 %; $C_{13}H_{19}ON_2BF_4$ requires: C 51.0, H 6.2, N 9.2 %

that were moderately soluble in ethanol, acetone and warm benzene but insoluble in ether and light petroleum (b.p. 60 to 80°).

2,5-*Di*-n-*decyloxybenzenediazonium chloride.* Prepared from 2,5-di-*n*-decyloxyaniline hydrochloride (8.1 g) in ethanol (650 cm^3) and sodium nitrite (2.1 g) in water (6 cm^3) with concentrated hydrochloric acid (30 cm^3), this derivative (8.0 g) was obtained as long needles. Crystallisation from benzene gave lemon-yellow prisms which softened at 78° and decomposed at 88°.

Found: N 6.0, Cl 7.9 %; $C_{26}H_{45}O_2N_2Cl$ requires: N 6.2, Cl 7.9 %.

It was insoluble in ether, water or light petroleum. Reduction with hypophosphorous acid gave *p*-di-*n*-decyloxybenzene.

When a larger proportion of water was used in the above preparation the diazonium salt crystallised from solution and then reacted with the free amine giving *4-amino-2,5-2′,5′-tetradecyloxyazobenzene* (47 %) which was crystallised from ethanol as lustrous brown plates, m.p. 100 to 101°.

Found: C 76.2, H 11.0, N 5.7 %; $C_{52}H_{91}O_4N_3$ requires: C 76.0, H 11.1, N 5.1 %.

The *hydrochloride* was a dark purple crystalline powder with a green reflex, m.p. 132 to 134°.

Found: C 72.5, H 10.5, N 4.8, Cl 4.2 %; $C_{52}H_{92}O_4N_3Cl$ requires: C 72.8, H 10.7, N 4.9, Cl 4.2 %.

2-*Amino*-4,5-3′,4′-*tetra*-n-*decyloxyazobenzene.* This derivative was formed when 3,4-di-*n*-decyloxyaniline hydrochloride (1 g) in ethanol (40 cm^3) was mixed with amyl nitrite (0.3 g) in ethanol (3 cm^3) at 4°. A precipitate formed and this was collected after 12 h (0,4 g), extracted with benzene and the extract chromatographed on alumina. The red band which was formed gave 2-*amino*-4,5-3′,4′-*tetra*-*n*-*decyloxy*-*azobenzene* as red prisms from benzene-light petroleum (b.p. 60 to 80°), m.p. 115 to 116°.

Found: C 76.3, H 10.8, N 4.7%; $C_{52}H_{91}O_4N_3$ requires: C 76.0, H 11.1, N 5.1%.

p-n-*Decylsulphonylbenzenediazonium toluene*-p-*sulphonate.* This derivative was obtained when concentrated hydrochloric acid (5 cm^3) was added to a mixture of sodium nitrite (0.53 g) in water (3 cm^3) and *p*-*n*-decylsulphonylaniline (1.5 g) in ethanol (100 cm^3) at 15°. After 10 min the solution which was formed was filtered, mixed with toluene-*p*-sulphonic acid monohydrate (1.5 g) in water (100 cm^3), and cooled to 0°. The diazonium toluene-*p*-sulphonate was precipitated as a white, difficultly filterable solid, m.p. 94° dec.

Found: C 57.2, H 6.7%; $C_{23}H_{32}O_5N_2S_2$ requires: C 57.5, H 6.7%.

o-n-*Decyloxybenzenediazonium fluoborate.* This salt (2.2 g) was prepared from *o*-*n*-decyloxyaniline hydrochloride (2.86 g). It was crystallised from a mixture of ethyl acetate and light petroleum (b.p. 60 to 80°) as pale yellow prisms, m.p. 68°, which were readily soluble in cold benzene.

Found: C 55.6, H 7.4, N 8.3%; $C_{16}H_{25}ON_2BF_4$ requires: C 55.2, H 7.2, N 8.1%

β-Naphthol Couplings

a) Wt. of diazonium salt = 133.4 mg (3.83 × 10^{-4} g mol).
Wt. of β-naphthol = 57.7 mg (4.00 × 10^{-4} g mol).
Wt. of pyridine = 50.4 mg (6.38 × 10^{-4} g mol).
Volume of reaction mixture = 50 ml.

Table 5

Time (min)	Optical Density	Azo body in diluted solution mg/50 ml	Azo body in reaction mixture g mol/litre × 10^3
0	0.000	0.000	0.00
7	0.069	0.208	0.26
14	0.102	0.299	0.37
20	0.126	0.370	0.46
53	0.202	0.586	0.73
118	0.351	1.011	1.25
166	0.450	1.291	1.60
223	0.557	1.598	1.98
309	0.670	1.931	2.39
503	0.885	2.531	3.13
3000	1.430	4.080	5.00 *

* This figure corresponds to 66% of the theoretical maximum concentration of azo compound.

b) Wt. of diazonium salt = 135.2 mg (3.89 × 10^{-4} g mol).
Wt. of β-naphthol = 28.4 mg (1.97 × 10^{-4} g mol).
Wt. of pyridine = 50.4 mg (6.38 × 10^{-4} g mol).
Volume of reaction mixture = 50 ml.

Table 6

Time (min)	Optical Density	Azo body in diluted solution mg/50 ml	Azo body in reaction mixture g mol/litre × 10^3
9	0.027	0.088	0.10
18	0.038	0.118	0.15
41	0.064	0.191	0.24
71	0.085	0.253	0.29

c) Wt. of diazonium salt = 132.5 mg (3.81 × 10^{-4} g mol).
Wt. of β-naphthol = 112.3 mg (7.80 × 10^{-4} g mol).
Wt. of pyridine = 50.4 mg (6.38 × 10^{-4} g mol).
Volume of reaction mixture = 50 ml.

Table 7

Time (min)	Optical Density	Azo body in diluted solution mg/50 ml	Azo body in reaction mixture g mol/litre × 10^3
8	0.204	0.591	0.73
19	0.327	0.943	1.17
41	0.650	1.860	2.30
71	0.960	2.750	3.40

d) Wt. of diazonium salt = 66.4 mg (1.91 × 10^{-4} g mol).
Wt. of β-naphthol = 56.8 mg (3.94 × 10^{-4} g mol).
Wt. of pyridine = 50.4 mg (6.38 × 10^{-4} g mol).
Volume of reaction mixture = 50 ml.

Table 8

Time (min)	Optical Density	Azo body in diluted solution mg/50 ml	Azo body in reaction mixture g mol/litre × 10^3
7	0.049	0.151	0.187
16	0.074	0.221	0.273
43	0.128	0.382	0.474
70	0.172	0.500	0.620

e) Wt. of diazonium salt = 271.2 mg (7.79 × 10^{-4} g mol).
Wt. of β-naphthol = 58.0 mg (4.03 × 10^{-4} g mol).
Wt. of pyridine = 50.4 mg (6.38 × 10^{-4} g mol).
Volume of reaction mixture = 50 ml.

Table 9

Time (min)	Optical Density	Azo body in diluted solution mg/50 ml	Azo body in reaction mixture g mol/litre × 10^3
8	0.099	0.293	0.36
16	0.148	0.431	0.59
41	0.242	0.701	0.87
74	0.313	0.901	1.11

The Coupling of 1-D-2-Naphthol

Wt. of diazonium salt = 133.7 mg (3.84 × 10^{-4} g mol).
Wt. of 1-D-2-naphthol = 56.7 mg (3.91 × 10^{-4} g mol).
Wt. of pyridine = 50.4 mg (6.38 × 10^{-4} g mol).
Volume of reaction mixture = 50 ml.

Table 10

Time (min)	Optical Density	Azo body in diluted solution mg/50 ml	Azo body in reaction mixture g mol/litre × 10^3
1.5	0.033	0.105	0.13
7	0.072	0.216	0.27
15	0.108	0.314	0.39
34	0.163	0.481	0.60
85	0.273	0.789	0.98
137	0.393	1.131	1.40
230	0.520	1.491	1.85
315	0.648	1.860	2.30

The Coupling to β-Naphthol in Benzene in the Presence of Tetra-n-butylammonium Hydroxide

Wt. of diazonium salt = 133.4 mg (3.84×10^{-4} g mol).
Wt. of β-naphthol = 57.7 mg (4.00×10^{-4} g mol).

N/10 Tetra-*n*-butylammonium hydroxide dissolved in a mixture of benzene (9 vol) and methanol (1 vol) was added in the amounts stated in the first column (4.0 ml = 4.00×10^{-4} g mol). The total volume of the reacting solution was 50 ml.

Table 11

Volume of N/10 Tetra-*n*-butylammonium hydroxide solution (ml)	Amount of Azo-compound formed after 1 min (mg)	Yield %
0.40	15.75	10.5
0.60	23.90	15.4
0.80	29.50	19.0
1.00	40.75	26.2
1.20	45.20	27.7
1.40	57.50	37.0
1.60	68.50	44.1
1.80	77.00	49.6
2.00	90.00	58.0
2.20	91.50	59.0
2.40	98.00	63.2
2.60	105.0	67.7
2.80	115.0	74.1
3.00	121.0	78.0
3.20	132.0	85.1
3.60	135.0	87.0
3.80	142.0	90.1

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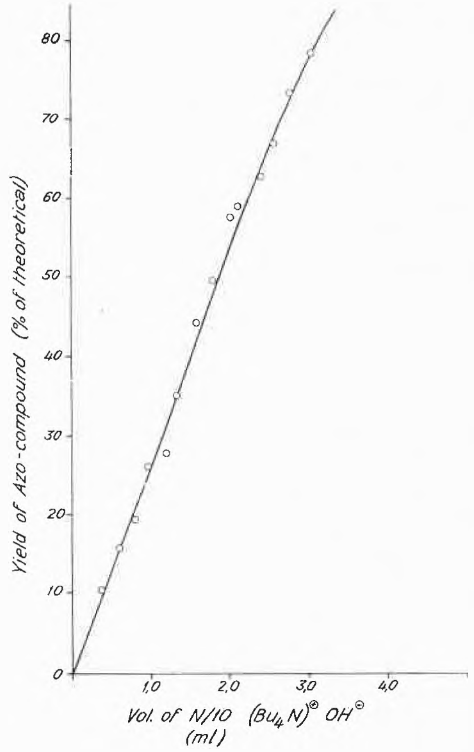

Fig. 2. Relation between the amount of azo-compound formed and the volume of N/10 tetra-*n*-butyl ammonium hydroxide added