examined by them, the yield of coupling product was less than that observed with phenyllithium, and in the case of o-tolyllithium the yield of bi-o-tolyl was 5% and the yield of o-cresol, 54%.

Experimental Part

The suspension of 4.5 g. of phenyllithium in 100 cc. of benzene, prepared in a nitrogen atmosphere, was oxidized by dry air, free of carbon dioxide, at 10-15°. A negative color test[6] was obtained in about ten hours. The phenol was characterized as 2,4,6-tribromophenol, and the p-phenylphenol as the acetate.

In three experiments the yields of phenol were 25.9, 23.1, and 22%; of biphenyl, 25, 23.7 and 22.6%; and of p-phenylphenol, 0.05, 0.06 and 0.05 g., respectively. The extent of the Wurtz–Fittig reaction with the bromobenzene is quite slight, for only 0.12 g. of biphenyl was isolated from the benzene washings of a 0.1 mole run.

(6) Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
IOWA STATE COLLEGE
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4,4'-Diaminodiphenylmethane as a Reagent for the Identification of Monobasic Saturated Aliphatic Acids

BY A. W. RALSTON AND M. R. McCORKLE

4,4'-Diaminodiphenylmethane has been found to give diamides of aliphatic acids by heating the theoretical proportions of the diamine with the respective acids.

$$CH_2\left(\underset{}{\bigcirc}NH_2\right)_2 + 2RCOOH \longrightarrow$$

$$CH_2\left(\underset{}{\bigcirc}NHCR\right)_2 + 2H_2O \\ \qquad\qquad\quad O$$
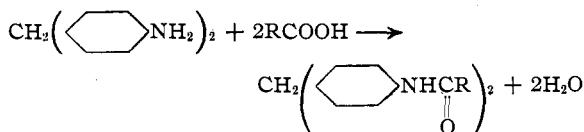
Because of the ease of preparation and purification and their high melting points, these compounds serve as excellent derivatives for the identification of aliphatic acids. With the lower members there was considerable depression of mixed melting points but this became increasingly smaller as the series was ascended.

In order to establish the structure of the diamides prepared by this method, the diamides of acetic, propionic and lauric acids were prepared from the diamine and either the anhydrides or the acid chlorides. These gave no depression of mixed melting points with the corresponding com-

pounds prepared from the acids. p,p'-Methylenebisacetanilide has been prepared previously from acetic anhydride and 4,4'-diaminodiphenylmethane.

Experimental

A mixture of 1 g. (0.005 mole) of 4,4'-diaminodiphenylmethane[1] and slightly more than 0.01 mole of the respective acid were mixed in a large Pyrex test-tube and heated at the boiling temperature until water ceased to be evolved. With the lower members of the series a reflux condenser was used and the period of heating was approximately one hour. The time necessary to complete the reaction decreased with the higher members of the series and in the case of stearic acid five minutes is sufficient. The products were crystallized to a constant melting point from a mixture of benzene and methanol except with some of

TABLE I

CONSTANTS OF DIAMIDES OF 4,4'-DIAMINODIPHENYL-METHANE

Acid	M. p., °C. (corr.)	Mixed m. p. with next highest homolog	N Analyses, % Calcd.	Found
Acetic[a,b]	227–228	205–210		
Propionic	212–213	188–193	9.03	9.33
Butyric	197–198	185–188	8.28	8.58
Valeric	188–189	179–181	7.65	7.92
Caproic	185–186	179–181	7.10	7.46
Heptylic	183–184	176–178	6.64	6.86
Caprylic	182–183	176–179	6.22	6.53
Pelargonic	176–177	175–177	5.83	6.11
Capric	178–179	173–175	5.54	5.93
Undecylic	175–176	172–174	5.25	5.45
Lauric[c]	174–175	171–173	4.99	5.38
Tridecylic	172–173	170–172	4.78	5.12
Myristic	170–171	167–169	4.53	4.73
Pentadecylic	167–168	166–168	4.34	4.36
Palmitic	167–168	164–166	4.15	4.39
Margaric	164–165	163–165	3.99	4.40
Stearic	164–165		3.83	4.12

[a] In order to purify this sample it was necessary to dissolve it in ethanol and add alkali until basic to phenolphthalein. Upon dilution with water and crystallization from benzene and methanol the product, m. p. 227–228°, was obtained. [b] Stoedel and Hause, Ber., **23**, 2577 (1890); Rivier and Farine, Helv. Chim. Acta, **12**, 865 (1929); Parkes and Morley, J. Chem. Soc., 315 (1936); Butler and Adams, THIS JOURNAL, **47**, 2617 (1925), reported m. p. 236–237°. [c] The authors are indebted to Mr. W. M. Selby for the samples of lauric, myristic and stearic acids. The remainder of the acids were obtained from the Eastman Kodak Company.

(1) The 4,4'-diaminodiphenylmethane used was prepared by crystallization from petroleum ether of Eastman Kodak Co. (practical), 4,4'-diaminodiphenylmethane, m. p. 90–91.5°. The melting point was 92–93°.

the higher derivatives where the methanol was replaced by *n*-butanol.

RESEARCH LABORATORY OF
ARMOUR AND COMPANY
CHICAGO, ILLINOIS   RECEIVED MARCH 25, 1939

The Colloid Chemistry of Leaf and Flower Pigments and the Precursors of the Anthocyanins

BY ROBERT ROBINSON AND GERTRUDE M. ROBINSON

In an interesting memoir[1] under the above title, W. D. Bancroft and J. E. Rutzler, Jr., have attributed views to us which we do not hold, the divergence being largely one of emphasis and due to generalization from the particular. These authors contrast the idea of Willstätter that anthocyanins result in nature from the reduction of flavonols with our supposed hypothesis that they normally originate from the oxidation of leucoanthocyanins.

We are aware that Willstätter (and Everest also) showed that flavonols could be reduced in the laboratory to anthocyanidins, but are not certain that he founded any general theory of biogenesis on these observations. It may be that we have overlooked a statement of this kind. For our own part it has been made abundantly clear that we do not regard the ordinary anthocyanins as derived from leuco-anthocyanins. Here it should be interpolated that by leucoanthocyanin (idin) we do not mean the colorless pseudo-bases or the readily oxidizable hydrocyanidin of Kuhn, but a special widely distributed class of natural products which are somewhat hard to convert into anthocyanidins, and are recognized by this transformation *in vitro* under certain conditions. Not one of the true leuco-anthocyanins (idins) has been isolated but cyanomaclurin and peltogynol are similar substances. Until they have been purified and characterized by analysis it is idle to speculate on their state of oxidation. A suggestion of a possible structure for a leuco-anthocyanidin having the same state of oxidation as cyanidin has been advanced.[2] Some leuco-anthocyanins undoubtedly are in a lower state of oxidation and it is to these alone that we consider the biogenetic oxidation hypothesis applies.

It is true that we have stated that oxidation *in vitro* is a more likely process than reduction

but this was an argument against the flavonol theory and it was not coupled with adherence to any general oxidation theory, though we can understand how a misconception of our attitude could arise.

As the concentration of leuco-anthocyanins cannot be determined independently, and in view of the possibility of disproportionation, it is hard to devise a sound experimental test for the oxygen requirement in any particular case. In some examples we can see that an oxidizing agent *is* necessary; the negative results cannot be interpreted unambiguously.

The following citation[3] explains our view of the part played by leuco-anthocyanins:

"Inevitably the transformation of these substances (leuco-anthocyanins) into coloring matters of flavylium type must occur in nature occasionally, but it does not follow that this route represents the standard mechanism. Two dihydroanthocyanidins, namely, cyanomaclurin and peltogynol, have been isolated and characterized; these are stabilized by the possession of a glucoselike oxide ring, and the related anthocyanidins are not found in the form of naturally occurring anthocyanins. The true leuco-anthocyanidins usually afford cyanidin on hydrolysis and autoxidation.

"It is too early to attribute a predominant role to the leuco-anthocyanidins, but it is already safe to assume that their modification represents an auxiliary pigmentation process. It is possibly operative in autumnal reddening and in the coloration following injuries or decortication of leaves."

Analogously we do not wish to exclude even flavonol reduction in *special* cases; we think there is ample evidence that it is not the *usual* mechanism of phytosynthesis.

We have consistently maintained that the anthoxanthins, and anthocyanins are formed in the plant from a common progenitor by forking of the roads. Furthermore, we discern a C_6 unit and a C_6–C_3 unit and assuming an origin from carbohydrate have pointed out that cyanidin represents the normal state of oxidation. This hypothesis was first advanced in 1921[4]; it has been developed in various lectures and publications.[5] The

(1) Bancroft and Rutzler, THIS JOURNAL, **60**, 2738 (1938).
(2) Robinson and Robinson, *Biochem. J.*, **27**, 207 (1933).

(3) Robinson and Robinson, *Nature*, **137**, 172 (1936).
(4) British Association Report, 89th Meeting, Edinburgh, p. 417.
(5) Ref. 3 and Report of the IXth International Congress of Pure and Applied Chemistry, Madrid, Vol. V, 1934, p. 25. *Proc. Univ. Durham Philosophical Society*, **8**, (i), 17 (1927–1928).