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New Synthetic Tools in the Pyridine, Quinoline and Other Nitrogen-Heterocyclic Series

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DYES CONTAINING LONG-CHAINED ALIPHATIC RADICALS

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The investigation of the synthesis and properties of compounds containing long-chained aliphatic radicals has been extended to the preparation of several azo dyes, coupling products of β—naphthol with the appropriately substituted aromatic diazonium chlorides. The dyes prepared include those from a series of three *p*—alkoxyanilines, $ROC_6H_4NH_2$, where R is *n*—$C_{12}H_{25}$—, *n*—$C_{14}H_{29}$—, and *n*—$C_{16}H_{33}$—, all deep red in color; and two brighter red compounds from *p*—(N—alkylsulfonamido)—anilines, $H_2NC_6H_4SO_2NHR$, where R is *n*—$C_{12}H_{25}$— and *n*—$C_{18}H_{37}$—.

These compounds are crystalline solids, soluble in the usual organic solvents and in fats and oils. The melting points of the compounds are such that they might serve as derivatives for the corresponding anilines.

The compounds prepared and their melting points are: 1—(*p*—dodecoxyphenylazo)—2—naphthol, m. 80-82°; 1—(*p*—tetradecoxyphenylazo)—2—naphthol, m. 81.5-83°; 1—(*p*—hexadecoxyphenylazo)—2—naphthol, m. 82-84°; 1—[*p*—(N—dodecylsulfonamido)—phenylazo]—2—naphthol, m. 163-164°; and 1—[*p*—(N—octadecylsulfonamido) — phenylazo]—2—naphthol, m. 158-159.5°.

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NEW SYNTHETIC TOOLS IN THE PYRIDINE, QUINOLINE AND OTHER NITROGEN-HETEROCYCLIC SERIES

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The halogen-metal interconversion reaction now makes possible the preparation of hitherto difficultly or completely inaccessible organolithium compounds from the corresponding bromo- or iodo-nuclear substituted nitrogen heterocycles by means of other organolithium compounds like *n*—propyllithium and *n*—butyllithium:

$$C_5H_4NBr + n\text{—}C_4H_9Li \longrightarrow C_5H_4NLi + n\text{—}C_4H_9Br$$

(3-bromopyridine) (3-pyridyllithium)

These organolithium compounds of the nitrogen heterocycles are of a relatively high order of reactivity with other functional groups.

Some of the types reported on in the pyridine series are:

1. 3—pyridyllithium in 70 per cent yield from 3—bromopyridine and *n*—butyllithium,
2. 3—quinolyllithium in 52 per cent yield from 3—bromopyridine,
3. 5—bromo—3—pyridyllithium in 41 per cent yield from 3, 5—dibromopyridine and slightly more than two equivalents of *n*—butyllithium.

In the carbazole series, some of the organolithium compounds reported are:

1. N—ethyl—2, 8—dilithiocarbazole in 84-91 per cent yield from N—ethyl—2, 8—dibromocarbazole, and in 79-92 per cent yield from the corresponding di-iodo-compound.
2. N—ethyl—2—lithiocarbazole [1] from the corresponding iodocarbazole in 68 per cent yield.

[1] Studies by Irving Banner.

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DIRECT SYNTHESES OF AMIDES FROM LONG-CHAINED ALIPHATIC AMINES

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An examination has been made of direct procedures for the synthesis of amides. Dodecylamine, tetradecylamine, hexadecylamine and octadecylamine have been treated with a variety of aliphatic and aromatic acids. Direct heating of the amine and acid, in open containers and at elevated temperatures, gave quite satisfactory yields of amides.

This direct procedure has been resolved into two stages. First, a mixture of amine and acid, dissolved or suspended in warm petroleum ether, gives promptly and in good yield the corresponding salt. These salts can be used for the characterization of amine and acid. Second, when the salts are heated they are converted to the amides.