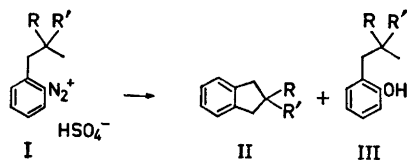


## A New Diazonium Ion Ring-Closure Reaction

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Diazonium salts derived from *o*-alkylanilines, with a chain-length of at least three carbon atoms, have been found to yield indane derivatives as well as the expected *o*-alkylphenols when undergoing thermal decomposition in aqueous acid solution. In Table 1 the preliminary yields are reported.



- I, II, III a R = R' = H  
 I, II, III b R = H, R' = CH<sub>3</sub>  
 I, II, III c R = R' = CH<sub>3</sub>

The alkyylanilines were prepared from the corresponding alkylbenzenes by nitration,<sup>1</sup> careful separation of the isomers on a spinning-band column, and reduction of the *o*-nitroalkylbenzenes with hydrazine hydrate (Pd/C catalyst).<sup>2</sup> The anilines were all gas chromatographically pure and had spectral and physical properties in accordance with reported values.

The diazotisations were made in 6 N sulphuric acid with sodium nitrite, whereupon the diazonium salt solution was poured into boiling 18 N sulphuric acid and the products were separated by steam distillation. GLC analyses of the raw products gave the figures reported in Table 1. Column chromatography on alumina with hexane followed by chloroform as eluents yielded the analytically pure products. Indane,<sup>3</sup> 2-methylindane,<sup>4</sup> 2,2-dimethylindane,<sup>5</sup> as well as *o*-propylphenol,<sup>6</sup> and *o*-isobutylphenol<sup>7</sup> are all reported in the literature, and a comparison of spectral and physical properties established the nature of the products.

Table 1. Composition of products from *o*-alkylbenzenediazonium sulphate.

Diazonium ion I	Product composition (%)		Total recovery (%)
	Indane II	Phenol III	
a <i>o</i> -propyl	13	87	100
b <i>o</i> -isobutyl	35	65	90
c <i>o</i> -neopentyl	88	<sup>d</sup>	60

<sup>d</sup> The rest of the product was composed of several compounds and has not been fully characterized.

This new carbon-carbon bond-forming reaction was first observed during the diazotisation of 2,4,6-trineopentylaniline, which had been made from 1,3,5-trineopentylbenzene. The properties of the single observable product, 2,2-dimethyl-4,6-dineopentylindane, will be published together with other derivatives of 1,3,5-trineopentylbenzene.<sup>8</sup>

The increase in the yields of the indanes with increasing branching in the hydrocarbon chain can be explained by hindrance to attack by the competing water nucleophile. It is also a well-known fact that alkyl substituents on a chain assist in ring-closure.<sup>9</sup>

When the reactions with isobutyl- and trineopentylaniline were performed in D<sub>2</sub>SO<sub>4</sub>/D<sub>2</sub>O, no deuterium was incorporated into the resulting indanes. In this case the steam distillation in the work-up procedure was excluded and the products were extracted from the reaction mixture.

This intramolecular alkylation reaction seems to have some analogies in the literature, but no real equivalence.

The Pschorr<sup>10</sup> coupling reaction to yield a bridged biaryl and the Meerwein<sup>11</sup> intermolecular arylation of an olefin, are well-known diazonium ion reactions. There are, however, many points of difference between these two reactions and this new one between a diazonium ion and a saturated hydrocarbon side chain. A closer comparison can be made with the reported formation of fluorenes upon diazotisation of 2-amino-2'-alkylbiphenyls.<sup>12</sup> The formation of phthalimidines upon *o*-amino-*N*,*N*'-dialkylbenzamidines<sup>13</sup> is another example.

From a mechanistical point of view there may be some similarities to the recently reported<sup>14</sup> intramolecular alkylation of an *o*-*t*-butyl group in the 2,4,6-tri-*t*-butylbenzyl carbonium ion.

Various models of the reaction mechanism are being considered and tested. The generation of a phenyl cation from the diazonium ion during thermal decomposition in aqueous acid seems well established.<sup>15</sup> This cation might undergo an intramolecular hydride ion transfer to generate an alkyl cation with subsequent ring closure.<sup>13</sup> Another and perhaps preferable working hypothesis is that the phenyl cation effects an intramolecular electrophilic substitution of hydrogen upon an aliphatic carbon atom. The attack may be either a back lobe attack<sup>14</sup> at the cationic carbon by the  $sp^3$  orbital of a C-H bond or an attack by the front lobe<sup>16</sup> of the  $sp^3$  orbital, where the electron density is greatest. If one of the two last-mentioned mechanisms will prove to be correct it will constitute one of the very rare  $S_E2$  reactions at a saturated carbon in a hydrocarbon chain. A possible "three-center" *intermediate*, with the characteristics of a non-classical carbonium ion, can be rejected as there was no deuterium incorporation into the indane. A comparison with the unaccepted one-step mechanism for electrophilic aromatic substitution also makes this last model less probable even as a transition state.

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## Correction to "The Fluorescence Properties of Vitamin A and their Changes during Photodecomposition"\*

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On p. 2518, para. 1, lines 2 and 3, the quantum efficiency of all-*trans* vitamin A<sub>1</sub> alcohol and acetate should read 0.067 and 0.068 instead of 0.67 and 0.68.

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