

## Short Communications

### Structure and Decomposition of Aryldiazoureas

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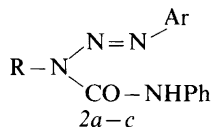
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Since 1888 it has been known that 1,3-disubstituted triazenes react with isocyanates under formation of diazoureas.<sup>1</sup> The reaction has been widely used in determination of the tautomeric structure of triazenes. The proposed mechanism was that the isocyanate reacted at the nitrogen with the hydrogen atom and that the structure of the diazourea could be established from analysis of the decomposition products, *i.e.* the *N,N'*-disubstituted urea as depicted in Scheme 1 reaction path A. Argumentation of that type has long been known to be unreliable and we will here show that in this case the decomposition products depend on how the decomposition is carried out.

**Results.** *N*-Aryldiazoureas are formed by reaction of phenyl isocyanate with equivalent amounts of triazene at room temperature in toluene or light petroleum solution.



1a–c



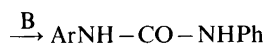
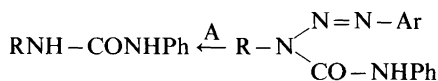
Compound	R	Ar
a	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>
b	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>
c	CH <sub>3</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>
d	C <sub>2</sub> H <sub>5</sub> OCOCH <sub>2</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>

The structure of the *N*-aryldiazoureas 2 could be established from the <sup>13</sup>C NMR spectra by observing

the quaternary carbon atoms in the *p*-tolyl group. From compound 2a and 3,3-dimethyl-1-*p*-tolyl-triazene<sup>2</sup> the chemical shifts for the two types of *p*-tolyl groups could be established. The *p*-tolyl diazo group is found at δ 146.3 and 138.8 and the *p*-tolylamino group at δ 139.3 and 132.6. For 2b the two quaternary carbon atoms in the *p*-tolyl group are found at δ 146.2 and 139.1, for 2c at δ 146.7 and 138.9 and for 2d at δ 145.8 and 139.5. The amino type *p*-tolyl group is not seen in the spectra and thus the structure for the diazoureas must be *N*-alkyl-*N*-aryldiazo-*N'*-phenylurea as shown for 2b–d.

The “*p*-tolyl method”<sup>3</sup> where discrimination between *p*-tolylamino and *p*-tolylimino is based on the <sup>1</sup>H NMR chemical shift of the *p*-methyl group turned out to be less useful here because the chemical shifts of the two types of methyl groups were of approximately the same value.

The decomposition of the *N*-aryldiazoureas was carried out in refluxing benzene with equivalent amounts of acetic acid and diazourea. Only the ureas formed were isolated and characterized. In all cases the urea after reaction path B was formed, in contrast to our expectations from the structure 2.

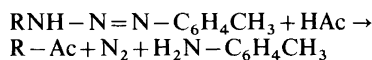
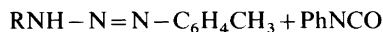
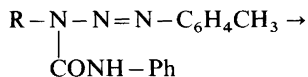


Scheme 1.

Decomposition of 2b in aqueous hydrochloric acid,<sup>1</sup> however, follows path A giving small amounts of *N*-benzyl-*N'*-phenylurea and no *N*-phenyl-*N'*-*p*-tolyl-urea. From these findings the structure was established as 2b.<sup>1</sup> Decomposition studies of that type can thus only be used in structure determination when the mechanism of the decomposition is fully understood. In this case, it seems possible that the phenyl isocyanate is split off first and the triazene decomposed afterwards. This is supported by the fact that a smell of phenyl isocyanate has been noticed<sup>4</sup> from the decomposition mixture and when the decomposition is carried out in refluxing xylene without acetic acid an IR absorption at 2300 cm<sup>-1</sup> is seen, corresponding to the phenyl iso-

cyanate. Finally, when the decomposition of 2b is carried out in benzene with equivalent amounts of aniline and two equivalents of acetic acid 66 % of *N,N'*-diphenylurea and 13 % *N*-phenyl-*N'*-*p*-tolylurea are formed.

The reason why no *N*-alkyl-*N'*-phenylureas are formed in the decomposition carried out in benzene with acetic acid may be explained by the fact that the alkyl group reacts with acetic acid with ester formation<sup>5</sup> when the triazene is decomposed. (Scheme 2).



Scheme 2.

*Experimental.* The experimental equipment was reported earlier.<sup>6</sup> All the aryldiazoureas have been prepared in accordance with a previously published procedure.<sup>1</sup>

*General procedure for decomposition of N-aryldiazoureas.* The diazourea (0.01 mol) was refluxed in benzene (50 ml) with acetic acid (0.01 mol) until the diazourea had disappeared (TLC). The reaction mixture was cooled in ice and the *N*-phenyl-*N'*-*p*-tolylurea filtered off.

*N'-Phenyl-N-p-tolyl-N-p-tolyldiazourea* 2a. M.p. 120 °C (d). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.33 (3 H, s), 2.38 (3 H, s), 6.87–7.72 (13 H, m), 8.56 (1 H, s) gave 84 % yield of *N*-phenyl-*N'*-*p*-tolylurea in the decomposition.

*N'-Benzyl-N-phenyl-N-p-tolyldiazourea* 2b. M.p. 120 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.36 (3 H, s), 5.36 (2 H, s), 6.92–7.69 (14 H, m), 8.42 (1 H, s) gave 62 % yield of *N*-phenyl-*N'*-*p*-tolylurea in the decomposition.

*N'-Methyl-N-phenyl-N-p-tolyldiazourea* 2c. M.p. 95 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.39 (3 H, s), 3.48 (3 H, s), 6.90–7.70 (9 H, m), 8.42 (1 H, s) gave 53 % of *N*-phenyl-*N'*-*p*-tolylurea in the decomposition.

*N'-Ethoxycarbonylmethyl-N-phenyl-N-p-tolyldiazourea* 2d. M.p. 88 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.23 (3 H, t), 2.37 (3 H, s), 4.15 (2 H, q), 4.86 (2 H, s), 6.87–7.73 (9 H, m), 8.35 (1 H, s) gave 75 % of *N*-phenyl-*N'*-*p*-tolylurea in the decomposition.

*Acknowledgement.* We are indebted to Statens Naturvidenskabelige Forskningsråd for <sup>1</sup>H and <sup>13</sup>C NMR facilities.

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