

### 3-Acyl-1-aryltriazenes. Preparation and Structure

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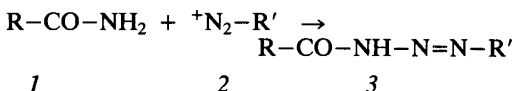
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Acylaryltriazenes were first synthesized by Alfred Bertho in 1927 from benzoyl azide and phenylmagnesium bromide.<sup>1</sup> Since then only a few acylaryltriazenes have been mentioned.<sup>2-4</sup> Oddo and Algerino<sup>2</sup> prepared acetylphenyltriene from acetamide and benzenediazonium chloride and described the product as an example of *besonders schöner fall von mesohydrischer isomerie* with a proposed bridge-bonded hydrogen atom. Ito and Fukuyama<sup>3</sup> prepared benzoylphenyltriazenes from nitrosobenzene and benzohydrazide.

Formyl-*p*-chloro- and formyl-*p*-bromophenyltriene, as precursors for diazoisocyanides,<sup>4</sup> were prepared in an ether-water mixture at neutral pH by coupling the diazonium ion with formamide. The obtained triazenes were described as reasonably stable in contradiction to reports<sup>2</sup> of formylphenyltriazenes isolated from aqueous solutions.

In spite of the doubt which has been cast upon the applicability of the method of Oddo and Algerino<sup>2</sup> for the preparation of acetyltriazenes<sup>5</sup> we report that formyl-, acetyl- and benzoyltriazenes can be prepared by their method.

Triazene formation from diazonium ions and amides were interesting as an extension of our work with triazenes.<sup>6,7</sup> The presence of a carbonyl group attached to nitrogen could change the normal tautomer distribution and the reaction of diazonium ions with nitrogen atoms less nucleophilic than amine nitrogen has not been thoroughly investigated and could be used as a model for reaction with proteins.



Scheme 1. Compound, R,R': a, CH<sub>3</sub>, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; b, C<sub>6</sub>H<sub>5</sub>, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; c, H, *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>; d, H, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; e, H, *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>; f, H, *p*-ClC<sub>6</sub>H<sub>4</sub>; g, H, *p*-BrC<sub>6</sub>H<sub>4</sub>; h, CH<sub>3</sub>, *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>; i, CH<sub>3</sub>, *p*-C<sub>2</sub>H<sub>5</sub>OCOC<sub>6</sub>H<sub>4</sub>; j, CH<sub>3</sub>, *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>; k, C<sub>6</sub>H<sub>5</sub>, *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>.

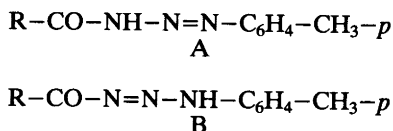
The attempts to prepare formyl-, acetyl- and benzoyltriene by coupling diazonium ion with the respective amide in aqueous sodium hydroxide solution was carried out as depicted in Scheme 1.

The coupling reaction is fairly good for acetamide giving *3a*, but gave low yields for formamide and benzamide (*3c* and *3b*). For all other reactions no triazene was characterized.

Application of the procedure for preparation of *3d* and *3e* gave rather unstable compounds decomposing vigorously upon heating to 80 °C. In CHCl<sub>3</sub> solution they decompose rapidly at room temperature, in DMSO solution slowly, which is why they were not characterized further. Attempts to obtain NMR spectra of these compounds in order to establish their tautomeric structure failed. However, it turned out that formyl-*p*-methoxyphenyltriene *3c* was stable at room temperature in solution. The method did not work for preparation of acetyl- (*3j*) and benzoyl-*p*-methoxyphenyltriene *3k*. No triazene was isolated presumably owing to much faster decomposition of the diazonium ion compared with the coupling reaction. We also tried to prepare formyl-*p*-chlorophenyltriene *3f* and formyl-*p*-bromophenyltriene *3g* by coupling the relevant diazonium ion with formamide in sodium hydroxide solution. On account of the reported stability<sup>3</sup> we hoped to obtain a stable product but in both cases the explosive compounds which are believed to be bis-*p*-halogenophenyldiazo ether ((X-C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>O)<sup>6</sup> were formed presumably owing to the electrophilic character of these diazonium ions. *3f* and *3g* could not be isolated even by reaction at slightly alkaline or at neutral pH. The attempts at making acetyl-*p*-nitrophenyl- (*3h*) and acetyl-*p*-(ethoxycarbonyl)phenyltriene *3i* gave two compounds in high yields, but the compounds were unstable, giving off nitrogen immediately after they were filtered off. They were not characterized.

The actual tautomeric structure of the acylaryltriazenes A or B could be established by observing the <sup>13</sup>C chemical shift values for the quaternary carbon atoms in the *p*-substituted phenyl groups.

For the *p*-tolyl groups the chemical shift values for the two quaternary carbon atoms are normal-



Scheme 2.

ly seen<sup>6,7</sup> for *p*-tolylidazo (A) at 146.3 and 138.8 ppm and for *p*-tolylamino (B) at 139.3 and 132.6 ppm. For compound 3a we find 139.0 and 146.3 ppm and for compound 3b 139.5 and 146.3 ppm, both in accordance with the tautomeric structure A. For compound 3c the chemical shift values are 141.7 and 160.2 ppm for the quaternary carbon atoms. These values are also in accordance with structure A as the use of substitution constants<sup>9</sup> for 4-methyl and 4-methoxy groups gives calculated values of 146.5 and 137.7 ppm for the *p*-tolyl group.

All three acyltriazenes were weak acids which could be dissolved in diluted sodium hydroxide and reprecipitated by adding diluted hydrochloric acid.

*Experimental.* The experimental<sup>10</sup> equipment was reported earlier. Melting points are uncorrected.

*General procedure for preparation of 3-acyl-1-aryltriazenes.* A solution of the diazonium chloride was prepared from amine (0.1 mol), hydrochloric acid (0.3 mol) in water (100 ml) and sodium nitrite (0.1 mol) in water (30 ml). The diazonium chloride solution was added dropwise to a stirred mixture of amide (0.20 mol), sodium hydroxide (0.20 mol) and water (100 ml) at 0 °C. After addition the mixture was stirred for 15 min and the foaming brown precipitate filtered off. The filtrate was acidified with hydrochloric acid and the triazene filtered off, dried and recrystallized from toluene–light petroleum.

*3-Acetyl-1-p-methylphenyltriazene 3a.* Yield 23 %, m.p. 120–121 °C. Anal. C<sub>9</sub>H<sub>11</sub>N<sub>3</sub>O: C, H, N. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.35 (3 H, s), 2.43 (3 H, s), 7.10–7.70 (4 H, m), 10.88 (1 H, s). IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 3300 (m), 1710 (s), 1500 (s), 1380 (s), 1210 (s), 1150 (s). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 170.4, 146.3, 139.0, 129.8, 121.5, 21.5, 20.8.

*3-Benzoyl-1-p-methylphenyltriazene 3b.* Yield 7 %, m.p. 90–92 °C. Anal. C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O: C, H, N. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.37 (3 H, s), 7.05–8.05 (9 H, m), 10.53 (1 H, s). IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 3290 (m), 1690 (s), 1605 (m), 1475 (s). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 165.1, 146.3, 139.5, 132.5, 132.2, 129.9, 128.4, 121.7, 20.8.

*3-Formyl-1-p-methoxyphenyltriazene 3c.* Yield 6 %, m.p. 102 °C. Anal. C<sub>8</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>: C, H, N. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.85 (3 H, s), 6.82–7.75 (4 H, m), 9.16 (1 H, d), 10.30 (1 H, d). IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 3260 (w), 1715 (s), 1605 (m), 1495 (m). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 166.2, 160.2, 141.7, 123.0, 114.5, 55.4.

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