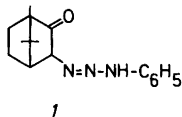


Aryl-2-oxo-3-bornyltriazenes and Aryldiazo-2-oxo-3-bornylureas. Rearrangement and Ring Closure

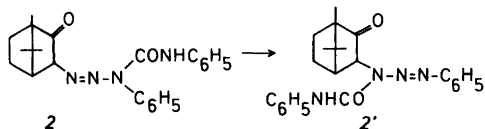
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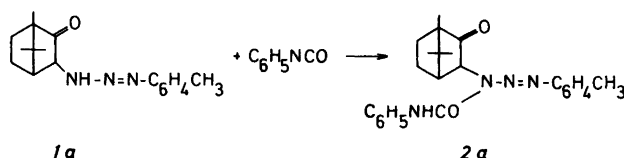
In connection with our work on triazenes^{1,2} the investigation of Forster and Garland³ attracted our interest. Their work is essentially an attempt to solve the problem about tautomerism in 1,3-disubstituted triazenes. They used the two methods of choice at that time, namely acid hydrolysis of the triazene and reaction of the triazene with phenyl isocyanate followed by acid hydrolysis of the diazourea. For the first time agreement is found between the two methods in structure elucidation of aliphatic-aromatic triazenes. They conclude that the structure of the triazene is 1-(2-oxo-3-bornyl)-3-aryltriazene (**1**) and that of the urea *N*-(2-oxo-3-bornyl)diazo-*N*-aryl-*N'*-phenylurea (**2**).



In addition they find an interesting reaction, namely that the 2-oxo-3-bornyldiazodiarylurea can rearrange to a compound with the same composition and they formulate the new compound as an *N*-aryldiazo-*N*-(2-oxo-3-bornyl)-*N'*-phenylurea (**2'**) which means that phenyl isocyanate has migrated from one nitrogen to another. (Scheme 1).



Scheme 1.

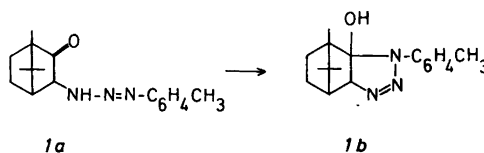


Scheme 3.

This rearrangement is mentioned by Cambell and Day in their review about the structure of triazenes⁴ and they suggest that the rearrangement may proceed through a cyclic intermediate.

We have repeated these experiments and found other structures for all three compounds in question. NMR and IR spectra of the alleged *N*-(2-oxo-3-bornyl)-*N'*-*p*-tolyltriazene which is formed by reaction of 3-amino-2-bornanon and *p*-tolylidiazonium chloride in aqueous solution show that mainly one isomer exists in solution. If another isomer is present the concentration must be below 5%. The IR spectrum shows that the 2-oxo-3-bornyl carbonyl absorption at 1740 cm⁻¹ is missing and so is the sharp NH stretching vibration at 3260 cm⁻¹ which is normally seen for 1,3-disubstituted triazenes.⁵

Instead a rather broad OH stretching absorption at 3130 cm⁻¹ is seen. From that evidence and from the knowledge that β -oxo-triazenes cyclize under formation of 4-hydroxy-1,2,3-triazolines⁶ we conclude that the triazene exists in a ring-closed form as **1b**. (Scheme 2).

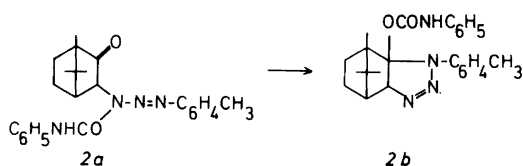


Scheme 2.

Reaction of **1b** with phenyl isocyanate gives a product with the expected composition of an aryldiazo-(2-oxo-3-bornyl)phenylurea. The TLC shows that the product consists of two compounds **2a** and **2b**. By recrystallization from light petroleum a compound **2a** can be isolated in pure form. The IR spectrum of **2a** shows an NH stretch absorption at 3350 cm⁻¹, a CO absorption at 1750 cm⁻¹ and a CONH amide I absorption at 1720 cm⁻¹. We therefore assume that there must be a small equilibrium concentration of **1a** in the solution and that phenyl isocyanate reacts with **1a** under formation of *N*-*p*-tolylidiazono-*N*-(2-oxo-3-bornyl)-*N'*-phenylurea **2a**. (Scheme 3).

Further evidence for structure **2a** is that the ^1H NMR spectrum shows signals corresponding to the 2-oxo-3-bornyl part of the molecule quite similar to those of 3-amino-2-bornanon and very different from the compound **1b**. Phenyl isocyanate reacts at N^3 in **1a** and not with N^1 which is seen from the ^{13}C NMR spectrum by observing the quaternary carbon atoms in the *p*-tolyl group. The two quaternary carbon atoms are normally seen^{1,2} for *p*-tolylidazo at 146.3 and 138.8 ppm and for *p*-tolylamino at 139.3 and 132.6¹ ppm. For compound **2a** we find 145.7 and 139.5 ppm in accordance with structure **2a**.

The other compound **2b** formed by reaction of **1b** with phenyl isocyanate can also be formed by rearrangement of **2a**. (Scheme 4).



Scheme 4.

The rearrangement of **2a** can be carried out in several ways. The rearrangement occurs even at room temperature in crystalline phase.³ A fast method which gives good yield is reflux in pyridine for a few minutes and then pouring the reaction mixture into water. The IR spectrum of the rearranged product shows dramatic changes from the IR spectrum of **2a**. The carbonyl band at 1750 cm^{-1} disappears. Instead an absorption at 1725 cm^{-1} , characteristic for carbonyl in carbamates,⁷ is seen. The ^1H NMR spectrum also shows substantial changes for the 2-oxo-3-bornyl part and the ^{13}C NMR spectrum shows that the carbonyl carbon atom found at 209.3 ppm in **2a** is missing in the rearranged compound **2b**. Instead a chemical shift at 154.1 ppm is seen which is in accordance with findings for the carbonyl carbon in isopropylphenylcarbamate of 154.0 ppm.⁸

An explanation of the rearrangement can therefore be that phenyl isocyanate is split from **2a**. The more stable **1b** is formed and phenyl isocyanate reacts catalyzed by pyridine with **1b** under formation of **2b**.

Experimental. The experimental equipment is reported earlier.¹ Melting points are uncorrected. All compounds have been prepared in accordance with previously published procedures.³

1b, m.p. 152–155 °C, yield 93%. Anal. $\text{C}_{17}\text{H}_{23}\text{N}_3\text{O}$: C, H, N. ^1H NMR (CDCl_3): δ 0.56–1.30 (14 H, m), 2.27 (3 H, s), 4.75 (1 H, d), 6.52 (1 H, s), 6.88–7.48 (4 H, m). IR (KBr, cm^{-1}):

3130 (s, broad), 2980 (s), 1520 (s), 1460 (s).

2a, m.p. 127–128 °C, yield 46%. Anal. $\text{C}_{24}\text{H}_{28}\text{N}_4\text{O}_2$: C, H, N. ^1H NMR ($\text{DMSO}-d_6$): δ 0.62–2.29 (14 H, m), 2.35 (3 H, s), 5.03 (1 H, d), 6.78–7.81 (9 H, m), 8.52 (1 H, b). IR (KBr, cm^{-1}): 3350 (w), 2950 (m), 1750 (s), 1720 (s).

2b, m.p. 185–186 °C, yield 80%. Anal. $\text{C}_{24}\text{H}_{28}\text{N}_4\text{O}_2$: C, H, N. ^1H NMR ($\text{DMSO}-d_6$): δ 0.55–1.69 (14 H, m), 2.33 (3 H, s), 4.50 (1 H, d), 6.90–7.76 (9 H, m), 8.51 (1 H, b). IR (KBr, cm^{-1}): 3320 (m), 2970 (m), 1725 (s).

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1. Treppendahl, S., Jakobsen, P. and Vernin, G. *Acta Chem. Scand. B* 32 (1978) 777.
2. Treppendahl, S. and Jakobsen, P. *Acta Chem. Scand. B* 34 (1980) 69.
3. Forster, M. O. and Garland, C. S. *J. Chem. Soc.* 95 (1909) 2051.
4. Cambell, T. W. and Day, B. F. *Chem. Rev.* 48 (1951) 299.
5. Simons, W. W. *The Sadler Handbook of Infrared Spectra*, Heyden, London 1978.
6. a. Mc Garrity, J. F. *Chem. Commun.* (1974) 558; b. Olsen, C. E. and Pedersen, C. *Acta Chem. Scand.* 27 (1973) 2279.
7. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, Methuen, London 1966.
8. Levy, C. G. and Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley, New York 1972.

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