

Dimethyläther III: Aus 100 mg I in 8 ml Aceton mit 0,1 ml Dimethylsulfat + 2 g K_2CO_3 unter Rückfluss während 8 Std., dann filtrieren, einengen und versetzen mit Wasser: gelber Niederschlag, der zur Entfernung von II in Chloroform gelöst, durch Aluminiumoxyd filtriert und anschliessend im Vakuum sublimiert wurde (200°, 0,001 Torr). Ausbeute 37 mg fast farblose Nadeln, Smp. 142°. – NMR. ($CDCl_3$): 3,86/3,90, 4,00 (je s, 3H), 3,96 (s, 9H), 6,74 (s, 1H), 6,95 (d, 1H), 7,7 (m, 2H). – IR.: 3010, 2940, 2840, 1622, 1608 cm^{-1} . – UV. (Methanol): λ_{max} (log ϵ) 242 (4,32), 330 (4,37) nm. – MS.: *m/e* 402 (M^+).

$C_{21}H_{22}O_8$ (402,39) Ber. C 62,68 H 5,51% Gef. C 62,87 H 5,64%

Alkalischer Abbau: 100 mg I in 20 ml Äthanol + 80 ml 50% KOH wurden unter N_2 während 48 Std. unter Rückfluss gekocht. Nach Abdampfen des Alkohols im Vakuum wurde durch die Lösung CO_2 geblasen, bis kein Niederschlag mehr entstand. Von diesem wurde abzentrifugiert. Die wässrige Phase wurde mit 5proz. HCl angesäuert und dann mit Äther extrahiert. Aus dem Extrakt erhielt man 14 mg Vanillinsäure. Die phenolische Fraktion bestand zur Hauptsache aus I.

LITERATURVERZEICHNIS

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156. The Relationship between C_6H_5N Isomers. Pyrolysis of Isatins¹⁾

by Curt Wentrup

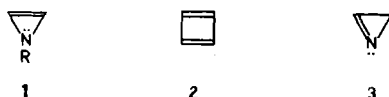
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Summary. The pyrolysis of methyl isatins is described. Examination of the toluidines formed by elimination of 2 CO followed by H-abstraction indicates that 1H-benzazirines (**12**) are intermediates. The interconversion of 1H- and 1aH-benzazirine (**15**) is not detectable. 1-Phenylbenzotriazole does not give a benzazirine intermediate.

1H-Azirines (**1**) being isoelectronic with cyclobutadiene (**2**), are expected to be antiaromatic, and reactions designed to produce them have given 2H-azirines (**3**) instead [1]. Recently, evidence was presented for the intermediate formation of **1** (R = phthalimido) in the pyrolysis of 1-phthalimido-1,2,3-triazoles [2].

Scheme 1



We reported previously that gas-phase pyrolysis of benzotriazoles (**4**) [3] [4] and isatin (**5a**) [3] gives 1-cyanocyclopentadienes (**6**) and anilines (**7**) via 1,3-biradicals (**8**)

¹⁾ Presented in part at the 4th Cork Mechanisms Conference, Kinsale, Co. Cork, Ireland, 4–9 April, 1971.

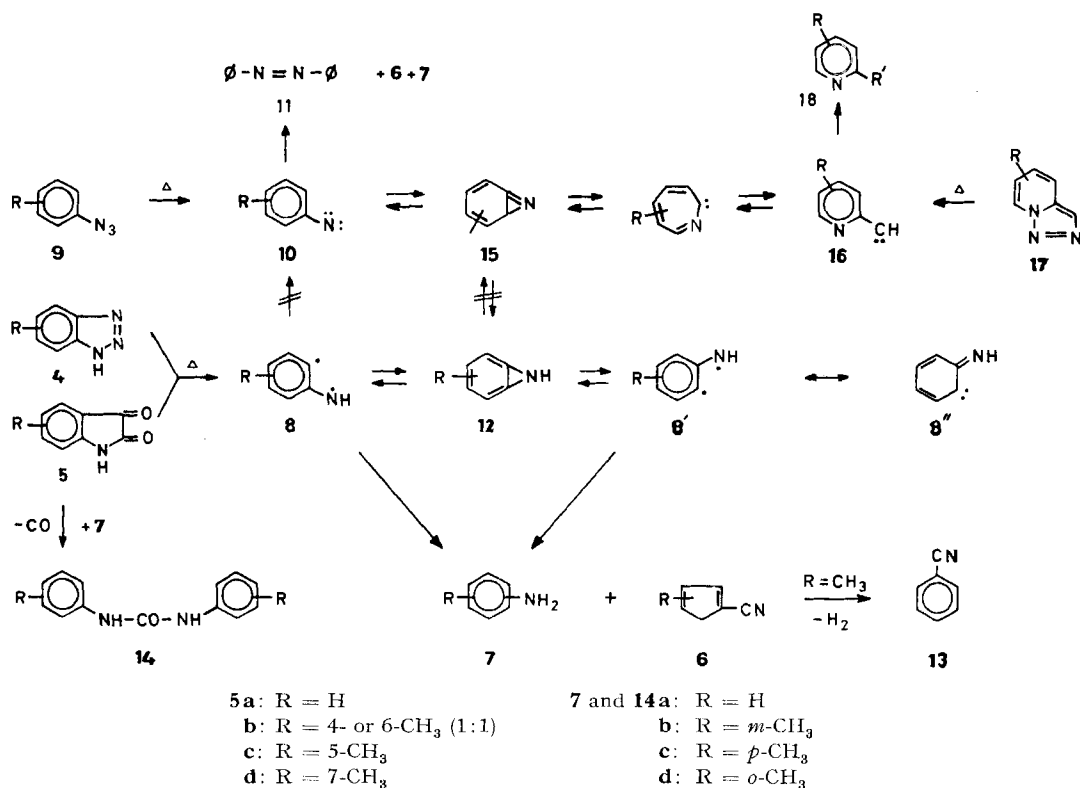
(mesomeric with iminocarbenes **8''**) (see Scheme 2). The same products (*inter alia*) are formed by pyrolysis of phenyl azides (**9**) [5] [6], but we have excluded the possibility of isomerization of **8** to phenylnitrene (**10**) [4], since azobenzene (**11**) was not produced from **8**. Furthermore, a deuteration study showed that the radical cations corresponding to **8** and **10** did not interconvert in the mass spectrometer [7].

We were interested in the possible intermediacy of 1*H*-benzazirine (7-aza-bicyclo-[4.1.0]hepta-1,3,5-triene) (**12**), formed by ring closure of the biradical **8**. The pyrolysis of benzotriazoles (**4**) [4] did not reveal any abundant existence of **12**; but benzotriazoles are not well suited for such a study because of their tautomeric nature which makes it impossible to locate H-N. Hence pyrolysis of e.g. 5(6)-methylbenzotriazole will *ipso facto* give both *m*- and *p*-toluidine.

The pyrolysis of the methyl isatins **5b-d** is now described (see Scheme 2). The products formed are given in the Table. The position of the methyl groups in the cyanocyclopentadienes (**6**) is not significant, since they isomerise under the reaction conditions, and also aromatize to benzonitrile (**13**) [4] [6].

For the carbanilides **14** whose formation is the subject of a separate study, only the major isomers are given; these were identified by IR. and m.p. comparison with authentic samples. The isomer distribution in the toluidines (**7**) was examined in detail by gas-chromatography and NMR.

Scheme 2



Pyrolysis of isatins **5b-d**

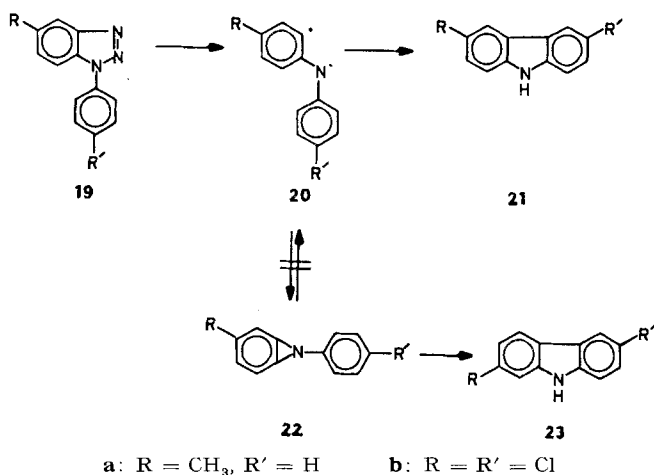
Compound	Temp. °C	Relative yield			Yield %					
		7b	7c	7d	7	6	13	14b	14c	14d
5b	900	95	2.5	2.5	7	3	51	1.3	-	-
5c	600	0	100	0	15	0.2	-	-	5.6	-
5c	900	6	94	0	7	2	52	-	1.3	-
5c	1100	6	94	0	0.06	0	18	-	-	-
5d	900	0	5	95	5.5	8	40	-	-	6.8

It is seen from the Table that isatins always give a major toluidine which is the one formed from an unrearranged biradical **8**, plus a minor toluidine which is the one expected from interconversion of the biradicals **8** and **8'** via the 1*H*-benzazirine **12** (see Scheme 2). Formation of the minor toluidine commenced at $\sim 700^\circ$, and the maximal yield was reached at $\sim 900^\circ$ (and remained stationary until 1100°) with 5-6% relative yield. Since the probabilities of **12** re-opening to either the original (**8**) or a new biradical (**8'**) are (nearly) equal, a 10-12% intermediacy of 1*H*-benzazirine (**12**) is indicated. Separate experiments showed that the toluidines did not interconvert at temperatures up to 1100° , and the isatins recovered from pyrolysis at 700° - 800° were unrearranged (at higher temperature pyrolysis was complete). If the methyl groups were migrating, a selective isomerization, as observed, would not be expected.

An isomer of **12**, namely 1*aH*-benzazirine (7-aza-bicyclo[4.1.0]hepta-2,4,6-triene) (**15**), has long been assumed to be an intermediate in the ring expansion reactions of phenylnitrene (**10**) [8] [9], and seems inevitable in the interconversion of phenylnitrene and 2-pyridylcarbene (**16**) [9]. Recently, it was postulated, in connection with the photolysis of anthranils, that the two benzazirines **12** and **15** exist in equilibrium at room temperature [10].

We have concluded that **12** and **15** do not thermally interconvert to any noticeable extent, since thermolysis of substituted phenyl azides (**9**) [6] [9] at temperatures up

Scheme 3



to 1000° have never produced positionally isomerised anilines, but only those expected from H-capture by the nitrenes **10**. However, since the equilibrium between **10** and **16** is strongly in favour of **10** [9], the yield of product arising through **15** could be low, and a partial interconversion of **15** and **12** might not be detected. More important is the fact that *vic*-triazolopyridines (**17**) which produce anilines and azobenzenes in high yields *via* **16**, **15** and **10** [9] do not give positionally isomeric anilines either; in this reaction **15** must be an important intermediate, and any significant isomerization to **12** would have been detected by the occurrence of isomeric anilines. The isomerization of **12** to **15** was also excluded by the absence of pyridine products and azobenzenes in the pyrolysis of isatins and benzotriazoles (products **18** and **11**).

The cyclization of the biradicals formed from 1-arylbenzotriazoles (e.g. **19** → **21**) is a well-known reaction [11] [12].

The involvement of benzazirine **22** in this system was excluded by the pyrolysis of **19a** at 780–1100°, when only 3-methylcarbazole (**21a**) and no 2-methyl-carbazole (**23a**) was produced. It has also been found that the benzazirine **22b** is not involved in the photolytic conversion of **19b** to **21b** [13]. This is presumably due to the rapidly occurring intramolecular reaction of the biradicals **20**, an escape route that is not open to the aminyls **8**.

Experimental Part

The pyrolysis apparatus and the analytical procedure has been described [14]; the packed tube was used. The isatins (0.5–3 g) were sublimed into the pyrolysis tube below their m.p. (140–200°) at 0.005–0.10 Torr. The products, collected in liquid N₂, were extracted with ether, distilled, and analyzed by gas chromatography on a 1.5 m × 5 mm column of 10% carbowax 20 M on Varaport 30 (Varian Associates) at 130° (injector 200°). Yields are given in the Table. The cyanocyclopentadienes (**6**) have been described previously [4]. The toluidine fractions were isolated by extraction of the products with 2N HCl, basification, and extraction with ether, and purified by column chromatography (Al₂O₃/CHCl₃). The isomer distribution was then examined by gas chromatography and NMR.

The dimethylcarbanilides (**14**) were left as white solids in the trap after washing with ether and CHCl₃. They were identified by IR., m.p. and mixed m.p. comparison with authentic samples.

It was found difficult to separate 4- and 6-methylisatin, prepared according to the literature [15]. This synthesis yielded a ca. 1:1 mixture (τ_{CH_3} 7.58 and 7.72) with m.p. 133–136°, which was pyrolysed as such (compound **5b**)².

Pyrolysis of isatin (**5a**) gave a) at 700°/0.15 Torr: 40% 1-cyanocyclopentadiene (**6a**), 10% aniline (**7a**) and 1.6% carbanilide (**14a**); b) at 600°/0.12 Torr: 15% **6a** and 15% **7a**; and c) at 500°/0.005 Torr: 6% **6a**, 3% **7a**, and ca. 0.15% nitrobenzene (decomposition incomplete).

p-Toluidine was pyrolysed at 1000–1100°/0.005–0.10 Torr and examined by gas chromatography as above. No *m*- and *o*-toluidine was detectable.

The pyrolyses of *m*-tolyl azide and 6-methyl-*vic*-triazolo[1,5-*a*]pyridine [6] [9] at 450–800° were re-examined. Analysis of the toluidine products as above showed that only *m*-toluidine was formed. Likewise *p*-tolyl azide gave only *p*-toluidine.

5-Methyl-1-phenylbenzotriazole (**19a**) [11] was pyrolysed at 780–1100°/10⁻³ Torr, being sublimed in at 150°. M.p. [11] and NMR. examination of the product indicated 3-methylcarbazole, but no 2-methylcarbazole²).

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²) This experiment was executed by Miss K. Wilczek.

