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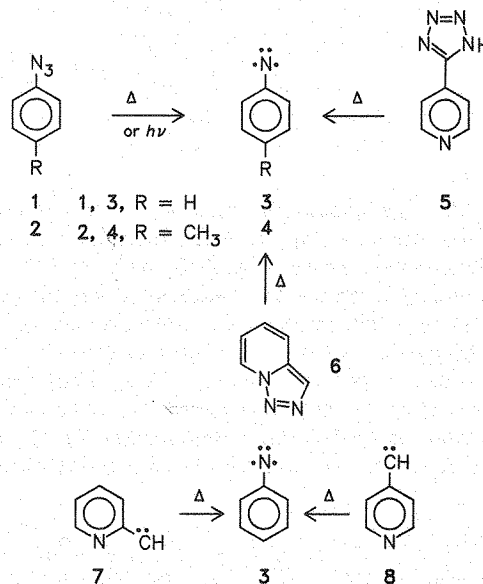
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## ESR Observation of Thermally Produced Triplet Nitrenes and Photochemically Produced Triplet Cycloheptatrienylidenes\*\*

By Martin Kuzaj, Holger Lüerssen, and Curt Wentrup\*

To date all nitrenes observed by ESR<sup>[1,2]</sup> have been generated by photolysis in low-temperature glasses or matrices. We now report the thermal gas-phase production of nitrenes with subsequent matrix isolation,<sup>[3]</sup> which permits direct monitoring of thermal carbene and nitrene rearrangements that were previously only inferred from product studies.<sup>[4]</sup> Moreover, we describe the first observation of cycloheptatrienylidenes and their aza derivatives.

The pyrolysis of phenyl azide **1** at 500°C gave a product with a strong ESR signal ( $|D/hc| = 0.9896$ ;  $|E/hc| = 0.00 \text{ cm}^{-1}$ ) typical of phenylnitrene **3**. The same signal was obtained on photolysis of matrix-isolated **1**. Phenylnitrene spectra were also obtained on pyrolysis of the *carbene* precursors **5** and **6**, thereby verifying the carbene-nitrene rearrangements **7** → **3** and **8** → **3**.<sup>[5,6]</sup> *p*-Tolynitrene **4** was similarly generated from *p*-tolyl azide **2** (Table 1). The much debated thermal cycloperambulation<sup>[7]</sup> to *m*- and *o*-tolynitrene did not take place to any measurable extent under these conditions.

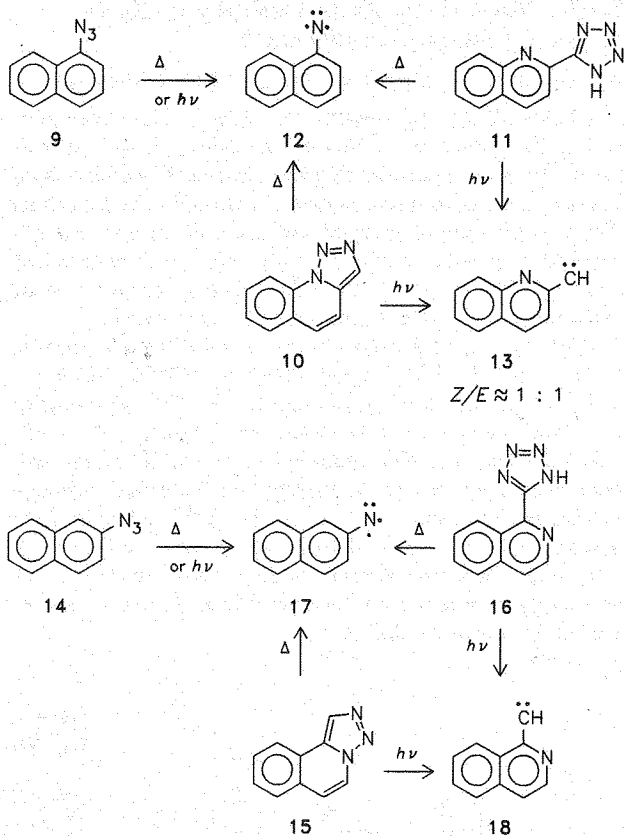


The discrete nitrenes **12** and **17** were likewise obtained from the naphthyl azides **9** and **14**, respectively, as well as

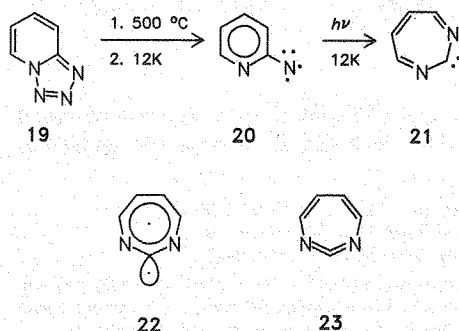
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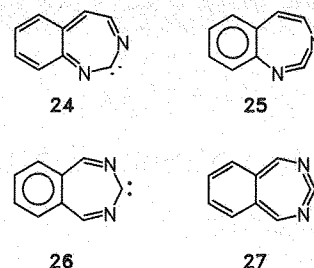
from the carbene precursors **10** and **11** or **15** and **16**. No interconversion of the 1- and 2-naphthylnitrenes **12** and **17** was observed. The carbenes **13**<sup>[8]</sup> and **18** were obtainable only on photolysis of the carbene precursors (Ar, 12 K). Both (*Z*) and (*E*) forms of **13** were observed, in a ca. 1 : 1 ratio. The fact that, in the thermal experiments, the carbene precursors rearrange entirely to nitrenes confirms our argument that nitrenes are intrinsically more stable thermodynamically than isomeric carbenes;<sup>[9]</sup> hence, the rearrangement of carbenes to nitrenes is virtually unidirectional in the gas phase.



The ring expansions interconverting carbenes and nitrenes are nowadays normally formulated in terms of cycloheptatetraenes/azacycloheptatetraenes.<sup>[2,4]</sup> The corresponding carbenes, the cycloheptatrienylidenes/azacycloheptatrienylidenes, have never been observed. If cycloheptatrienylidenes have triplet ground states,<sup>[10]</sup> it should be possible to generate such species by photolysis of triplet precursors. Indeed, this appears to have been achieved: Photolysis (200-W high-pressure Hg lamp) of thermally generated and Ar-matrix-isolated 2-pyridyl nitrene **20** gave



a new triplet carbene characterized by unusually low *D* and *E* values (Table 1). These values are too low for a heteroarylcarbene, because aza substitution tends to increase the *D* value (Table 1); therefore, the new carbene may be 1,3-diazacycloheptatrien-2-ylidene **21**, which would be strongly delocalized, as expressed in canonical structure **22**. The thermal (singlet) rearrangement of **20** (as monitored by IR spectroscopy) gives only the carbodiimide **23**, which is presumably the lowest-energy form of this seven-membered ring system.<sup>[11]</sup>



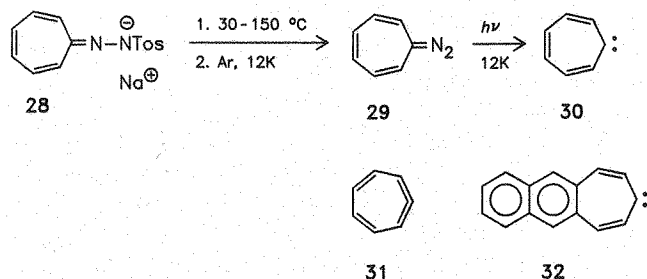
The structural assignment of **21** was tested by irradiation of 2-quinolyl- and 1-isoquinolyl nitrene; both gave the same carbene, **24**, which is also characterized by low *D* and *E* values (Table 1). 3-Isoquinolyl nitrene gave a different carbene, **26**. The corresponding carbodiimides **25** and **27** have been observed by IR spectroscopy.<sup>[4,11]</sup>

Table 1. ESR data for some nitrenes and carbenes [a].

Triplet species	$ D/hc $ [cm <sup>-1</sup> ]	$ E/hc $ [cm <sup>-1</sup> ]	Number of exp. [b]
<b>3</b> [c, d]	0.990(5)	0.0000(0)	4
<b>4</b> [d]	0.967	0.0000	1
<b>12</b> [c, d]	0.793(6)	0.0025(4)	7
<i>Z</i> - <b>13</b> [c]	0.531(1)	0.0265(2)	7
<i>E</i> - <b>13</b> [c]	0.467(0)	0.0259(2)	4
<b>17</b> [c, d]	0.925(2)	0.0023(3)	6
<b>18</b> [c]	0.489(1)	0.0245(2)	9
<b>20</b> [c, d]	1.051(8)	0.0000(0)	3
<b>21</b> [c]	0.426(2)	0.0056(2)	2
2-quinolyl nitrene [c-e]	1.034(2)	0.0039(1)	3
1-isoquinolyl nitrene [c-e]	0.847(2)	0.0042(1)	2
<b>24</b> [c]	0.386(1)	0.0150(0)	3
3-isoquinolyl nitrene [c-e]	0.943(2)	0.0049(1)	4
<b>26</b> [c]	0.433(0)	0.0124(0)	2
phenylcarbene [c, f]	0.517(1)	0.0245(2)	7
<b>30</b> [c]	0.425(0)	0.0222(2)	2
<b>32</b> [c]	0.453	0.0193	1
2-pyrazinyl nitrene [c-e]	1.014(2)	0.000	3
2-pyrimidinyl nitrene [c-e]	1.217(15)	0.0052(0)	4
4-quinolyl nitrene [c, d, g]	0.882(3)	0.0020(2)	5
2-quinoxalyl nitrene [c, e]	0.955(2)	0.0030(1)	2
2-quinoxalyl carbene [c, h]	0.474(0)	0.0261(1)	7

[a]  $H_0 = h\nu/g\beta \approx 3372.0$  Gauss; the exact value of  $\nu$  was measured in each experiment. Uncertainties in *D* and *E* values in units of the least significant digit. [b] Number of experiments used in averaging *D* and *E* and determining the uncertainties. [c] Photochemically produced. [d] Thermally produced. [e] From annelated tetrazoles or azides. [f] By photolysis of phenyldiazomethane or by pyrolysis of 5-phenyltetrazole followed by photolysis. [g] From 4-quinolyl azide or by thermal rearrangement of 2-quinoxalyl carbene produced by pyrolysis of either 1,2,3-triazolo[1,5-*a*]quinoxaline or 2-(5-tetrazolyl)quinoxaline. [h] Photolysis of triazoloquinoxaline or tetrazolylquinoxaline.

The above results led us to attempt the direct generation of triplet cycloheptatrienylidene **30**. Mild pyrolysis of the salt **28** gave the diazo compound **29** (IR: 2048 cm<sup>-1</sup>; Ar,



12 K). Photolysis of **29** at 12 K gave a carbene, different from phenylcarbene (Table 1) and characterized by a low *D* value. The ESR signal intensity did not follow the Curie law exactly, and, when the warmed sample was cooled again, the signals failed to return to their original intensities. One intriguing possibility is that **30** has a triplet ground state and, on warming, is partly converted into the lower-energy<sup>[10]</sup> allene **31**. Repeated warming and cooling should finally remove triplet **30** from the matrix.<sup>[12]</sup> Cyclohepta[b]naphthalen-8-ylidene **32**, a ground-state triplet,<sup>[13]</sup> was similarly generated and gave *D* and *E* values very close to those of **30** (Table 1).

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1, 622-37-7; 2, 2101-86-2; 3, 2655-25-6; 4, 38157-47-0; 5, 14389-12-9; 6, 274-59-9; 7, 21963-51-9; 8, 37998-87-1; 9, 6921-40-0; 10, 235-21-2; 11, 101772-02-5; 12, 3315-52-4; 13, 78759-52-1; 14, 20937-86-4; 15, 34456-69-4; 16, 59175-48-3; 17, 3315-51-3; 18, 101772-03-6; 19, 274-87-3; 20, 24843-39-8; 21, 101772-04-7; 24, 101772-07-0; 26, 101772-09-2; 28, 18870-24-1; 29, 101418-91-1; 30, 17476-70-9; 32, 73794-91-9; PhCH<sub>2</sub>·, 3101-08-4; PhCH=N<sub>2</sub>,

766-91-6; 5-phenyltetrazole, 18039-42-4; 2-quinolynitrene, 101772-05-8; 4-quinolynitrene, 101772-12-7; 1-isoquinolynitrene, 101772-06-9; 3-isoquinolynitrene, 101772-08-1; 2-pyrazolynitrene, 101772-10-5; 2-pyrimidinylitrene, 101772-11-6; 2-quinoxalylitrene, 101772-13-8; 2-quinoxalylcarbene, 101772-14-9; 2-(5-tetrazolyl)quinoxaline, 101772-15-0; 1,2,3-triazolo[1,5-*a*]quinoxaline, 13390-30-2.

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