

ADDUCTS OF NORBORNADIENE AND PHENYL AZIDE

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(Received in USA 20 March 1969; received in UK for publication 5 May 1969)

The 1,3-dipolar reaction of phenyl azide and norbornadiene could conceivably lead to eight adducts (1 - 8); two are 1:1 adducts (1,2) and six (3 - 8) incorporate two phenyl azide molecules for each norbornadiene molecule. Huisgen (1) has reported the isolation of one 2:1 adduct, assigned structure 4, and a red oil that apparently contained at least one 1:1 adduct. We have now isolated in crystalline form both 1:1 adducts (1,2), both exo-exo 2:1 adducts (3,4), and the exo-endo adduct 6 which has the phenyl groups in a trans relationship, and we have evidence that the second exo-endo adduct (5) is present in the reaction mixture, although we have not been able to isolate it. We have not been able to observe either endo-endo isomer (7,8), and we conclude that they constitute less than 2-3% of the reaction mixture.

When phenyl azide in cyclohexane was allowed to react with an excess of norbornadiene at 65° for two hours, a 67% yield of 1:1 adduct was obtained (a very small amount of 2:1 adduct was also formed) which afforded on fractional crystallization the exo isomer (1), m.p. 55°, and the endo isomer (2), m.p. 124°, in a ratio of 11:1. When slightly more than two equivalents of phenyl azide was used in the reaction, the yield of 2:1 adducts was essentially quantitative. This mixture afforded compounds 4 (m.p. 226° (decomp); Lit. (1) 236-8° (decomp)), 3 (m.p. 164-166°), and 5 and 6) in the ratio 13:5:1. Alternatively, when the endo 1:1 adduct 2 was allowed to react with phenyl azide, an 81% yield of 2:1 adducts was obtained. This was mainly 5 and 6 in the ratio 2:3, although the

TABLE  
 CHEMICAL SHIFTS ( $\tau$ )  
 COUPLING CONSTANTS (Hz)

Compound	CHEMICAL SHIFTS ( $\tau$ )				COUPLING CONSTANTS (Hz)							
	bridge-head (h)	endo (n)	exo (x)	bridge vinyl (v)	J <sub>hn</sub>	J <sub>hx</sub>	J <sub>nn'</sub>	J <sub>xx'</sub>	J <sub>vh</sub>	J <sub>vv'</sub>	J <sub>bb'</sub>	
1 ~	6.60 <sup>a</sup> 6.71 <sup>a</sup>	5.14 <sup>b</sup> 6.03 <sup>b</sup>	-	8.53 <sup>b</sup> 8.77 <sup>a</sup>	3.74 3.84	~0	-	9.5	-	3.0	6.0	10.0
2 ~	6.35 <sup>a</sup> 6.53 <sup>a</sup>	-	4.67 5.67	8.46 <sup>b</sup> 8.64 <sup>a</sup>	4.01 4.20	-	4.5 <sup>c</sup> 3.5 <sup>c</sup>	-	10.5	3.5	6.0	9.5
3 ~	6.71 <sup>a</sup> 6.96 <sup>a</sup>	5.17 (two) 6.05 (two)	-	8.87 <sup>a</sup> (two)	0	0	-	9.5	-	-	-	d
4 <sup>e</sup> ~	6.78 <sup>a</sup> (two)	4.91 (two) 5.82 (two)	-	8.92 <sup>a</sup> (two)	0	0	-	9.5	-	-	-	d
6 ~	6.65 <sup>f</sup> (two)	5.55 <sup>a</sup> 6.11 <sup>a</sup>	4.78 5.71	8.46 <sup>a</sup> 8.62 <sup>a</sup>	0 ~0	5.5 <sup>c</sup> 5.0	9.0	12.5	-	-	-	12.0

Spectra recorded in CDCl<sub>3</sub> (except 4) at 100 MHz. Chemical shifts are for the protons designated and each entry refers to one proton unless "two" is stated. Phenyl protons appeared in  $\tau$  2.4-3.1 region as a complex multiplet; signals corresponding to about one proton normally appeared as a distinct multiplet at the high field end of the range.

<sup>a</sup>Peaks broadened

<sup>b</sup>Appreciable splitting (1-2 Hz) besides that recorded in Table

<sup>c</sup>J values associated with exo proton of  $\tau$  value recorded on same line

<sup>d</sup>None observed

<sup>e</sup>Dilute pyridine-d<sub>5</sub> solution

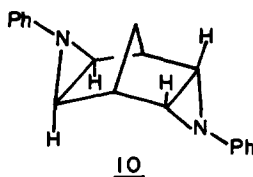
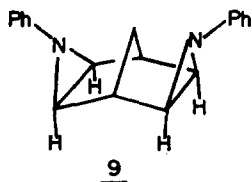
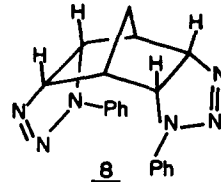
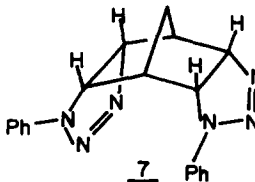
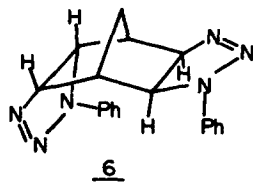
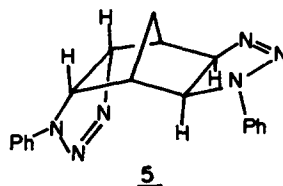
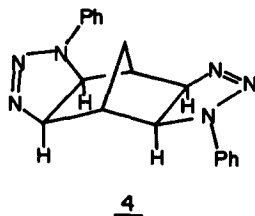
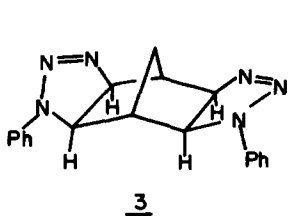
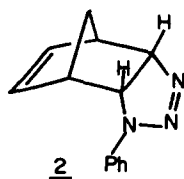
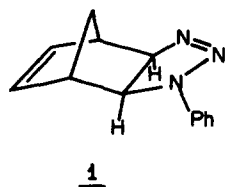
<sup>f</sup>Exceptionally broad and ill-defined

possibility that a small amount of endo-endo adducts was formed can not be excluded. It was possible to isolate a homogeneous sample of 6, m.p. 230° (decomp), but 5 was always obtained contaminated with 6.

Each isolable adduct had the appropriate composition (by combustion analysis) and ir and uv spectroscopic characteristics; mass spectrometry served to confirm the molecular formulae, but in each case the peak of highest observed mass was M-28 (representing loss of N<sub>2</sub> from the molecule). The structural assignments were then essentially a problem in nmr spectroscopy. The exo-endo assignments were based on the correlation (2) that the coupling constant between a bridgehead proton and an adjacent endo proton has a value near zero, while the corresponding value for an exo proton is in the range 3-6 Hz. The other structural features followed from the type of molecular symmetry required by the spectrum. The data used are shown in the Table. The spectrum of the mixture of 5 and 6 showed, in addition to the spectrum of 6, peaks at positions that would be expected for the protons of 5 on the basis of correlations with assignments in the Table, but it is not possible to make an analysis with any confidence.

Exposure to diffuse sunlight cleanly converted 3 or 4 to the same bisaziridine 9 (C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>), m.p. 182-186°, which showed, besides the phenyl protons at  $\tau$  2.6-3.4, only three signals as broadened single peaks at  $\tau$  7.06 (bridgehead protons), 7.57 (protons at positions 2,4,6,8) and 8.62 (bridge protons). However, under the same conditions 5 and 6 gave a complex mixture of products which, on the basis of the nmr spectrum of the mixture, may have contained some of the bisaziridine 10, but it has not yet been possible to verify this point by isolation of 10. Irradiation of the 1:1 adducts 1 and 2 led only to uncharacterizable tars and some recovered starting material. In agreement with Huisgen's report (1), we have found that heating 1 to 120° converts it to 1-phenyl-1,2,3-triazole and cyclopentadiene.

Acknowledgement. Discussions of this topic with Professor D. G. Farnum have been of considerable value to us. This work received financial support from the National Research Council (Canada) for which we are grateful.



## REFERENCES

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