Tetrahedron Letters No. 44, pp 3873 - 3874, 1977. Pergamon Press. Printed in Great Britain.

ON THE ISOLATION OF DIAZOCYCLONONATETRAENE

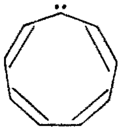
Edward E. Waali,[*,1] Jeffrey L. Taylor, and Neil T. Allison

Departments of Chemistry, Georgia College, Milledgeville, GA 31061 and

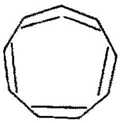
University of Wisconsin-Whitewater, Whitewater WI 53190

(Received in USA 18 July 1977; received in UK for publication 16 September 1977)

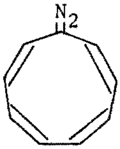
Our interest in cyclic, fully conjugated carbenes which have potential isomeric allene structures led us to the investigation of the 1-2 system. The logical precursor of 1 was the previously reported diazocyclononatetraene.[2] We have repeated the literature work and now conclude that the original structural assignment of the diazo compound is incorrect.



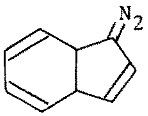
1



2

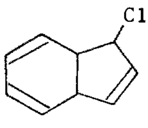


3

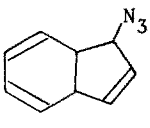


4

After a mixture of lithium cyclononatetraenide[3] and tosyl azide was stirred in THF at 25° for 24 hours, poured into water, extracted with ether, followed by drying and rotary evaporation of the solvent,[4] an infrared spectrum of the residue showed a new band at 2090 cm^{-1} in addition to one at 2113 cm^{-1} due to the excess tosyl azide. After chromatography through alumina or silica gel with petroleum ether, the 2090 cm^{-1} material (Compound A) was isolated in very low yield. This is the compound which was previously reported as 3.[2,5] Additional infrared features of interest were bands in the 3029 to 3070 cm^{-1} and 2850 to 2940 cm^{-1} regions. The latter, though, suggest a saturated carbon-hydrogen relationship. A reasonable alternative for Compound A might be the bicyclic diazo compound 4, since cyclononatetraenes easily undergo electrocyclic ring closures.[6] The pmr spectrum, though, ruled out this possibility since it showed the presence of three different saturated hydrogens in a pattern remarkably similar to that in 9-chlorobicyclo[4.3.0]nona-2,4,7-triene (5).[7] Finally, when the material was found to be stable in 1 M HCl, we were forced to rule out any other diazo structure for Compound A. A substance which did fulfill the ir, pmr and acid stability requirements was the azide 6.



5



6

An authentic sample of **6**,[8] prepared from the reaction of **5** with sodium azide in aqueous acetone, exhibited ir and pmr spectra[7] which were identical with those of Compound A. Therefore, the 2090 cm^{-1} band is due to an azide stretching vibration[9] and not a diazo vibration.

The mode of formation of **6** is not clear but it is a rather minor pathway.[10] When the reaction of the cyclononatetraenide ion and tosyl azide is conducted, a 44 % yield of evolved nitrogen gas is measured. The possible involvement of **3**, **4** and **1** in this reaction awaits our further determination.

Acknowledgment. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

REFERENCES AND FOOTNOTES

(1) Present address: University of Wisconsin-Whitewater

(2) D. Lloyd and N. W. Preston, *Chem. Ind.* (London), 1039 (1966).

(3) E. A. LaLancette and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 1941 (1965).

(4) We thank Professor Lloyd for the private communication of some experimental and spectroscopic details.

(5) The reported infrared value for this compound[2] was 4.85 μ but was later amended to 4.77 μ.[4] Our value (polystyrene calibrated) is 2090 cm^{-1} or 4.78 μ.

(6) For instance, P. Radlick and G. Alford, *J. Am. Chem. Soc.*, **91**, 6529 (1969).

(7) Pmr spectra (CCl$_4$, δ values): **5**: 3.19 ppm (d of m, 11.5 Hz, 1H, H$_1$), 3.70 (d of m, 11.5 Hz, 1H, H$_6$), 4.70 (m, 1H, H$_9$), and 5.3-6.0 (m, 6H, olefinic). **6**: 2.94 ppm (d of m, 10.9 Hz, 1H, H$_1$), 3.68 (d of m, 10.9 Hz, 1H, H$_6$), 4.18 (m, 1H, H$_9$), and 5.3-5.9 (m, 6H, olefinic).

(8) Anal. Calcd for C$_9$H$_9$N$_3$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.88; H, 5.74; N, 26.34.

(9) Aliphatic azides show a strong band close to 2100 cm^{-1}. See Y. N. Sheinker, L. B. Senyanvina and V. N. Zheltova, *Dokl. Akad. Nauk SSSR*, **160**, 1339 (1965); *Chem. Abstr.*, **63**, 152*h* (1965).

(10) It is conceivable that an intially formed triazine,[11] suffers sulfur-nitrogen bond cleavage, resulting in an azide transfer instead of the usual diazo transfer.

(11) See M. Regitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 733 (1967) for a review of the diazo transfer reaction.