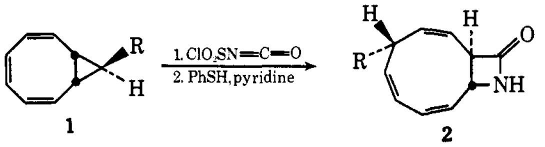
Crystal and Molecular Structure of *cis*-Bicyclo[6.1.0]nonatriene–Tetracyanoethylene Cycloadducts

Sir:

In previous papers[1] we have shown that addition of the highly reactive uniparticulate electrophile[2] chlorosulfonyl isocyanate to *cis*-bicyclo[6.1.0]nonatriene (**1a**) leads to the unique formation of trans-fused β-lactam **2a**. Of further mechanistic import were the companion observations that a similarly high level of stereocontrol was exhibited by the anti-9 substituted derivatives **1b** and **1c** which give rise only to **2b** and **2c**, respectively. The related syn isomers were totally unreactive under the conditions employed. A dipolar pathway involving initial attack by the electrophile at C-3 in the folded conformation of **1** (a geometry unattainable by the syn-9 substituted derivatives for steric reasons) with intermediate generation of *trans*-1,3-bishomotropylium ions or the structurally related pentadienyl cations has been advanced to account for these observations.[1]



1　**2**

a, R = H
b, R = CH$_3$
c, R = Cl

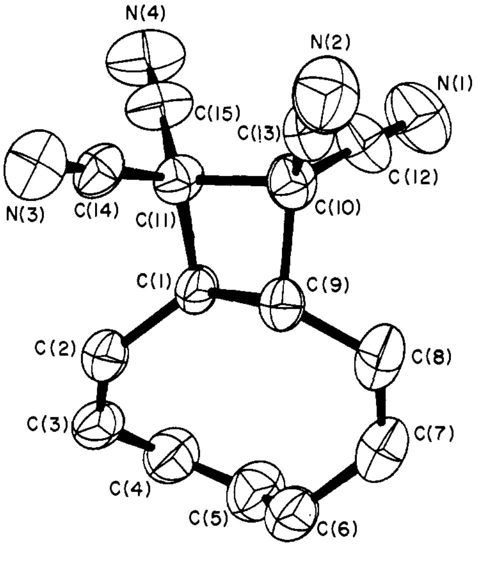
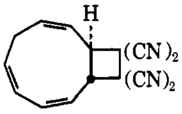
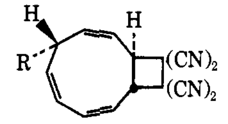


Figure 1. A structural view of **3** as determined by X-ray analysis showing the conformation of the molecule.

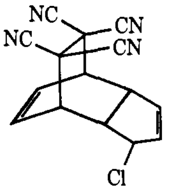
As an extension of this work, we have sought to examine the reactivity of other potential uniparticulate electrophiles with **1** and now report equally impressive stereochemical findings with tetracyanoethylene. The condensation of **1a** with TCNE had previously been recognized to lead to **3**,[3] but detailed knowledge of the ring juncture stereochemistry was not available. The nmr spectrum of **3** is of no assistance in this particular instance. The single-crystal X-ray diffraction analysis of **3** (Figure 1) now reveals clearly that the fusion of the nine- and four-membered rings is trans.



3



4a, R = CH$_3$
b, R = Cl



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When equimolar quantities of **1b** and TCNE were allowed to stand at 25° in tetrahydrofuran solution for 3.5 days (immediate red coloration on mixing), a lone adduct, mp 152–153°,[4] was obtained in 69% yield. The gross structure of this substance follows from its ultraviolet [$\lambda_{\max}^{C_2H_5OH}$ 231 nm (ϵ 11,240)] and nmr spectral data [$\delta_{TMS}^{CDCl_3}$ 5.1–6.5 (m, 6, olefinic), 4.45 and 4.00 (AB with small additional couplings, J_{AB} = 11 Hz, bridgehead), 3.4 (m, 1, $>CHCH_3$), and 1.13 (d, J = 7 Hz, 3, methyl)]. Unfortunately, this adduct did not afford crystals suitable for X-ray diffraction study. The nature of the ring juncture and the stereochemistry at C-6 are, however, supported by the marked spectral similarities to **4b** (see below).

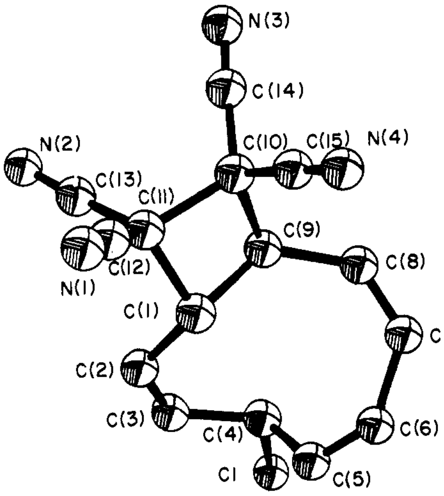

Figure 2. A structural view of **4b** as determined by X-ray analysis showing the conformation of the molecule.

In the case of the more labile 9-chlorobicyclo[6.1.0]-nona-2,4,6-triene, reaction with TCNE had been found earlier to give **5** in 50% yield.[5] In our hands, a sample of this chlorocarbon enriched in the anti isomer (anti/syn = 23/5) again led chiefly to **5**. However, careful processing of the mother liquors lent itself to the isolation of **4b**: mp 204–206°; $\lambda_{\max}^{C_2H_5OH}$ 226 nm (ϵ 11,110); $\delta_{TMS}^{CDCl_3}$ 5.4–6.6 (m, 7, olefinic and $>CHCl$)

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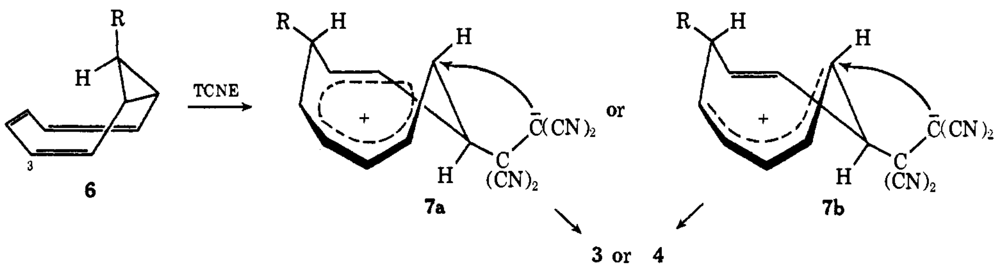
[1] (a) L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *J. Amer. Chem. Soc.*, **94**, 630 (1972); (b) L. A. Paquette and M. J. Broadhurst, *ibid.*, **94**, 632 (1972).

[2] L. A. Paquette, G. R. Allen, Jr., and M. J. Broadhurst, *ibid.*, **93**, 4503 (1971).

[3] (a) W. H. Okamura and T. W. Osborn, *ibid.*, **92**, 1061 (1970); (b) C. S. Baxter and P. J. Garratt, *ibid.*, **92**, 1062 (1970); *Tetrahedron*, 27, 3285 (1971).

[4] Satisfactory elemental analyses were obtained for the new compounds.

[5] E. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 1941 (1965).



and 4.4 (AB pattern, $J_{AB} = 11$ Hz, 2, bridgehead). The three-dimensional features of **4b** as unambiguously established by X-ray diffraction are shown in the computer-generated drawing given in Figure 2.[6]

With the structures of **3** and **4** now resolved, some commentary on their mechanism of formation appears in order. The possibility of concerted $({}_{\pi}2_s + {}_{\pi}2_s)$ cycloaddition to *cis*^{4}-cyclononatetraenes (conceivably present in low concentration) is not tenable for reasons of ring juncture stereochemistry and because of the negative control experiments of Baxter and Garratt.[3b] Nor is direct $({}_{\pi}2 + {}_{\pi}8)$ cycloaddition to **1**[3a] compatible with the structural data. Concerted $({}_{\pi}2_a + {}_{\pi}2_s)$ fusion to *cis*^{2},*trans*,*cis*-cyclononatetraene (thermally producible from **1**)[7] must likewise be considered inoperative because exclusive cis ring fusion in the adduct would result. Similarly, the postulate of stepwise ${}_{\pi}2 + {}_{\pi}2$ cycloaddition to this tetraene does not seem warranted because it is not entirely reconcilable with the high level of stereoselectivity associated with the substituent at C-6 in **4a** and **4b**. Rather, the above data, when taken in consort with our additional observations that only anti-9 and not syn-9 substituted bicyclo[6.1.0]-nonatrienes react with TCNE under the stated conditions, seemingly point again[1] to that pathway which involves initial electrophilic attack of TCNE at C-3 of the less stable bicyclononatriene tub conformation **6**. Generation of **7a** or **7b** is followed by C–C bond formation as shown to afford uniquely a trans-fused cyclobutane ring.

Earlier,[3] the capability of TCNE for nonconcerted cycloaddition to *cis*-bicyclo[6.1.0]nonatrienes with the formation of bifunctional dipolar ions was not considered. Yet, the ionic character of numerous TCNE cycloadditions to a variety of alkenes,[8] strained unsaturated hydrocarbons,[9] and cyclic polyolefins[10] is well recognized. In the particular case of **1**, the development of stabilizing electronic delocalization in intermediates **7a** and **7b**[1] apparently constitutes a significant driving force for the ionic pathway.[11]

(6) Complete details of the two X-ray analyses will be outlined in our full paper. All bond distances and angles agree well with generally accepted values. For **3**, full-matrix least-squares refinements converged smoothly to the present minimum of 8.5% for the conventional discrepancy index. In the case of **4b**, a relatively high *R* factor of 12.9% has been realized because of crystal decomposition which was detected in the check reflections but not corrected for.

(7) A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, **93**, 3083 (1971).

(8) P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970).

(9) See, for example: S. Nishida, I. Moritani, and T. Teraji, *J. Chem. Soc. D*, 36 (1971); J. E. Baldwin and R. E. Peavy, *J. Org. Chem.*, **36**, 1441 (1971); J. E. Baldwin and R. K. Pinschmidt, Jr., *Tetrahedron Lett.*, 935 (1971); R. Noyori, N. Hayashi, and M. Katô, *J. Amer. Chem. Soc.*, **93**, 4948 (1971).

(10) H.-P. Löffler, T. Martini, H. Musso, and G. Schröder, *Chem. Ber.*, **103**, 2109 (1970).

(11) This work was supported in part by the National Science Foundation (O. S. U.) and the U. S. Atomic Energy Commission (I. S. U.) whom we thank.

(12) Holder of a NATO Postdoctoral Fellowship (1970–1972) administered by the Science Research Council.

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Received November 5, 1971

Book Reviews

Advances in Molten Salt Chemistry. Volume 1. Edited by J. BRAUNSTEIN (Oak Ridge National Laboratory), GLEB MAMANTOV (University of Tennessee), and G. P. SMITH (Oak Ridge National Laboratory). Plenum Press. New York and London. 1971. xii + 284 pp. $17.50.

This new series will be a valuable reference to those working in the area of molten salts. Contributors and topics in this first volume are: R. E. Hester, University of New York, "Vibrational Spectroscopy of Molten Salts"; Y. Marcus, Hebrew University, "Liquid Extraction from Molten Salts"; C. R. Boston, Oak Ridge National Laboratory, "Molten Salt Chemistry of the Haloaluminates"; D. A. J. Swinkels, Broken Hill Proprietary Co., Ltd., New South Wales, Australia, "Molten Salt Batteries and Fuel Cells"; and J. W. Hastie, National Bureau of Standards, "Thermodynamic Studies, by Mass Spectrometry, of Molten Mixed Halide Systems."

Each article has been written as a review intended to bring the reader up to date in a particular area of molten salt research. Dates on literature references indicate that materials available through 1969 and some early 1970 work have been included.

Hester's article on vibrational spectra includes introductory theoretical material and a review of experimental techniques, both of which are helpful to the nonspecialist. Advantages and disadvantages of transmission, reflectance, and emission infrared methods are discussed as are various sources and cell designs. The section on results includes an interesting summary of complex species and polymers (involving groups II, III, and IVA and I, II, and IVB metals) which have been characterized with infrared and Raman spectra.

Chapter 2 on liquid extraction by Marcus also includes a treatment of introductory theory (mostly thermodynamic but some kinetics) and experimental technique. Data on miscibility gaps are given for binary systems (58 systems) and ternary systems with a