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1,4 ADDITION OF DICYANOCARBENE ONTO CYCLOOCTATETRAENE

A. G. Anastassiou and R. P. Cellura

Department of Chemistry
Syracuse University
Syracuse, New York 13210

and

E. Ciganek

Central Research Department, Experimental Station
E. I. DuPont de Nemours and Co., Inc.
Wilmington, Delaware[1]

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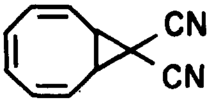
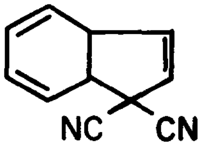
CARBENES and nitrenes very rarely add to polyenes in a 1,4 fashion, only two such cases having been reported to date.[2,3] Presently, we briefly demonstrate that one of the primary products in the reaction of thermally generated (ca. 80°) dicyanocarbene with cyclooctatetraene (COT) is in fact a 1,4 adduct.



1



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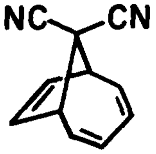

3

The reaction under discussion was recently reported to furnish two products characterized as 1 (70%) and 2 (18%).[6] Nevertheless, the less abundant component was assigned structure 2 only on a tentative basis and with considerable reservation since much of its chemistry was not deemed to be entirely as anticipated of a dihydroindene structure. It was noted[6] for example, that the compound neither reacts with methyl acetylenedicarboxylate at elevated temperatures nor does it aromatize when treated with various dehydrogenating agents under quite forcing conditions. These observations, coupled with the fact that the substance in question appears to be a primary reaction product[6,7] prompted us to re-examine the original structural assignment.

The nmr spectrum of this compound, determined at 220 MHz and shown in Figure 1, provides the desired structural information. In the first place, the presence of a single allylic resonance (H_1), doublet of doublets centered at τ 6.1 (2 H; J_{13} = 7.2 Hz, J_{12} = 1.5 Hz), demands that the molecule possess an element of symmetry and thus serves to eliminate 2 as a structural candidate. Secondly, the actual splitting of the high-field doublet (H_1) is such as to require that the allylic hydrogens be coupled 1. to a pair of identical and isolated ethylenic protons (H_2), doublet at τ 4.5 (2 H; J_{12} = 1.5 Hz), and 2. to a symmetrically disposed pair of olefinic protons (H_3), multiplet at τ 3.9-4.1 (2 H; J_{31} = 7.2 Hz, J_{34} = 12.2 Hz), which is also coupled to a similar pair of hydrogens (H_4), multiplet at 3.5-3.7 (2 H; J_{34} = 12.2 Hz). Finally, the uv spectrum of this molecule [$\lambda_{max}^{C_6H_{12}}$ 218 nm (ϵ 3900), 255 (4500), 264 (4400), 274 (sh) (2400)][6] strongly implicates the presence of a conjugated diene function. All available information, spectral and chemical, thus serves to single out structure 3 for the substance in question.[8]

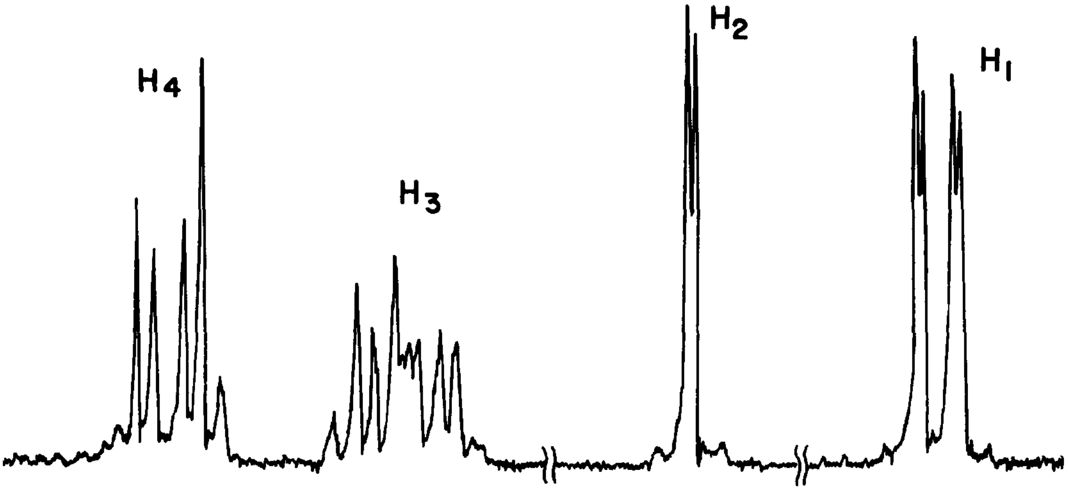

Figure 1. 220 MHz nmr spectrum of 3.

In terms of mechanism, we note that analogy with the closely related addition of cyanonitrene (NCN) to COT[4] would suggest that adducts **1** and **3** are chiefly produced from singlet and triplet dicyanocarbene respectively. Indeed, on conducting appropriate "variable-dilution" experiments we uncovered a significant parallel between the magnitude of the **1** to **3** ratio and the previously observed[6] loss of stereochemistry in the reaction of dicyanocarbene with either *cis*- or *trans*-2-butene which was shown to arise from an increase in the amount of triplet carbene with increasing dilution. Specifically, we find that the ratio of **1** to **3** changes from 3.9 in neat COT to 1.1 in 1:10 COT-cyclohexane to 0.3 in 1:100 COT-cyclohexane. This pronounced "dilution effect" coupled with the fact that the two adducts (**1** and **3**) do not interconvert at the reaction temperature, *requires that **1** and **3** arise chiefly from singlet and triplet* $C(CN)_2$ *respectively.*

Finally, we wish to draw attention to the single common characteristic between cyanonitrene and dicyanocarbene, *i.e.*, the cyano function. The rather unique tendency of this group to divert part of the reaction into the 1,4 pathway coupled with the distinct preference of the triplet to follow this course, suggests that 1,4 addition is actually observed here chiefly because of the ability of the substituent to stabilize the diradical intermediate and hence extend its lifetime to such an extent as to allow for closure to the 1,4 adduct.

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REFERENCES AND REMARKS

(1) Contribution No. 1738.

(2) For a timely and lucid monograph on the subject see: T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes and Arynes", Appleton-Century-Crofts, New York, N. Y., 1969.

(3) These are, (*a*) 1,4 addition of cyanonitrene to cyclooctatetraene[4] and (*b*) cycloaddition of phenylcarbene across the 9,10 carbons of anthracene.[5]

(4) A. G. Anastassiou, *J. Am. Chem. Soc.*, **87**, 5512 (1965); **90**, 1527 (1968).

(5) H. Nozaki, M. Yamabe and R. Noyori, *Tetrahedron*, **21**, 1657 (1965).

(6) E. Ciganek, *J. Am. Chem. Soc.*, **88**, 1979 (1966).

(7) Specifically, the minor product does not rearrange to **1** when heated at the reaction temperature (80°); it does so, however, slowly, at 160°.[6]

(8) Significantly, the product under study closely resembles the 1,4 adduct of NCN to COT both spectrally (nmr, uv) and in terms of its lack of reactivity with dienophiles.