CYCLOADDITION OF 3-PHENYLSYDNONE WITH CYCLOOCTATETRAENE

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<u>Abstract:</u> 3-Phenylsydnone reacts with cyclooctatetraene to give a 2:1-cycloadduct containing the dihydrobullvalene moiety as the major product.

During the past decade, the chemistry of cyclooctatetraene has received considerable attention and several reviews have appeared in the recent literature.^{1,2} Cyclooctatetraene has played a major role in many aspects of theoretical and synthetic chemistry.¹ As a medium-ring polyene, it undergoes a wide variety of reactions which are often accompanied by skeletal transformations, and it is also the progenitor of a large number of interesting ring systems. Cycloadditions of cyclooctatetraene with both electron deficient 2π and 4π -components have been extensively studied in recent years.^{1,3,4} In contrast, there are only a few examples in the literature dealing with the cycloaddition of cycloaddition of COT with mesoionic compounds such as sydnones. Sydnones are known to undergo reaction with olefins and acetylenes to give 2-pyrazolidines and pyrazoles, respectively.⁶ The reaction involves a 1,3-dipolar cycloaddition of the sydnone, behaving like a cyclic azomethine imine, to the corresponding acetylenic or olefinic dipolarophile followed by carbon dioxide evolution and aromatization or tautomerization. In this communication we wish to report on a novel reaction which occurs when 3-phenylsydnone (1) is allowed to react with cyclooctatetraene.

Heating a mixture of 3-phenylsydnone (<u>1</u>) and cyclooctatetraene in a sealed tube at 140°C followed by silica gel chromatography resulted in the formation of three products. The structure of the major product (<u>9</u>, 56%), mp 112-113°C, was assigned on the basis of its characteristic spectral properties; Anal. for $C_{23}H_{20}N_2$; m/e 324; uv (95% ethanol) 307 nm (ϵ 22800); NMR (400 MHz, CDCl₃) & 2.02 (<u>m</u>, 1H), 2.12 (<u>m</u>, 1H), 2.78 (<u>m</u>, 1H), 3.02 (<u>m</u>, 1H), 3.11 (<u>m</u>, 1H), 3.47 (<u>bs</u>, 1H), 3.57 (<u>bs</u>, 1H), 3.70 (<u>dd</u>, 1H, J=10.0 and 7.0 Hz), 4.11 (<u>bs</u>, 1H), 4.28 (<u>bs</u>, 1H), 5.73 (<u>t</u>, 1H, J=9.5 Hz), 5.95 (<u>dd</u>, 1H, J=10.0 and 4.5 Hz), 6.02 (<u>t</u>, 1H, J=9.5 Hz), 6.51 (<u>d</u>, 1H, J=10.0 Hz), 7.19 (<u>t</u>, 1H, J=7.3 Hz), 7.38 (<u>t</u>, 1H, J=7.6 Hz), 7.49 (<u>s</u>, 1H)

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and 7.60 (d, 1H, J=8.3 Hz); C¹³ NMR (20 MHz, CDCl₃) 26.2, 29.2, 33.3, 38.8, 44.7, 46.0, 67.2, 83.5, 117.6, 118.2, 119.9, 122.4, 125.4, 126.5, 127.0, 129.3, 132.8, 140.3 and 148.2. Cycloadduct <u>9</u> was unequivocally established by an X-ray single crystal structure analysis; Crystal Data: rhombohedral R₃,a=20.927(8)A⁰, α =118.68(3)⁰, Z=6, D_c=1.19 gm cm⁻³,f(000)=1106, $4.0^{\circ} \le 20 \le 109.0^{\circ}$. Using Ni filtered CuK α radiation, 2247 unique reflections were measured on a Nicolet R₃ four circle diffractometer with a 20-0 scan technique. The structure was solved by direct methods with the SHELX-76 program and refined to least squares to R=0.08 for all the data.⁷

The minor 2:1-cycloadduct $\underline{8}$ (10%), mp 161-162^oC, showed the following spectroscopic properties; Anal. for $C_{23}H_{22}N_2$; m/e 326 (M⁺); uv (95% ethanol) 307 nm (ε 13000) and 346 nm (ε 5900); NMR (90 MHz, CDC1₃) 6 1.76-2.50 (<u>m</u>, 4H), 2.85-3.60 (<u>m</u>, 6H), 4.20 (<u>dd</u>, 1H, J=9.5 and 8.0 Hz), 4.40-4.90 (<u>m</u>, 2H), 5.65-6.20 (<u>m</u>, 3H), 6.45 (<u>dd</u>, 1H, J=10.0 and 1.5 Hz) and 6.70-7.35 (<u>m</u>, 5H); C¹³ NMR (20 MHz, CDC1₃) 24.1, 31.5, 39.9, 41.0, 41.3, 41.6, 47.9, 55.3, 55.4, 95.4, 104.1, 119.8, 126.6, 127.4, 129.5, 137.2, 147.1, 150.3 and 174.0. Oxidation of <u>8</u> proceeded in reasonable yield to give cycloadduct <u>9</u>, thereby confirming its gross structure.

The 1:1-cycloadduct was assigned structure $\underline{5}$ (9%), mp 150-151°C, on the basis of the following data; Anal. for $C_{15}H_{14}N_2$; m/e 222 (M⁺); uv (carbon tetrachloride) 285 nm (ϵ 15400) and 360 nm (ϵ 3800); NMR (60 MHz, CDCl₃) δ 3.06 (\underline{dd} , 1H, J=9.0 and 3.5 Hz), 3.25 (\underline{d} , 1H, J=9.0 Hz), 3.73 (\underline{d} , 1H, J=9.0 Hz), 3.90 (\underline{dd} , 1H, J=9.0 and 3.5 Hz) and 6.9-7.80 (\underline{m} , 10H); C¹³ NMR (20 MHz, CDCl₃) 32.0, 48.0, 113.0, 119.0, 125.5, 128.5, 129.0, 133.0, 146.0, 149.0 and 180.0.

The formation of the above cycloadducts suggest that the mechanism shown in Scheme I is operative. Adducts $\underline{8}$ and $\underline{9}$ can be rationalized in terms of cycloaddition of sydnone $\underline{1}$ with cyclooctatetraene followed by carbon dioxide extrusion and a proton shift. The initially formed 1:1-adduct $\underline{7}$ undergoes a subsequent reaction with another molecule of cyclooctatetraene to give $\underline{8}$, which is eventually oxidized to $\underline{9}$. We believe that tautomer $\underline{6}$ is initially formed which then produces $\underline{7}$ by analogy with the reaction of COT with other 1,3-dipoles.⁵ It is, of course, possible, that $\underline{6}$ can be formed from bicyclooctatriene $\underline{2}$ via tautomer $\underline{3}$.⁸ An alternate path which can also account for the formation of $\underline{8}$ and $\underline{9}$ involves the reaction of





3-phenylsydnone with the 76[°] dimer of cyclooctatetraene.⁹ This dimer was formed under the reaction conditions and when heated with <u>1</u>, produced cycloadducts <u>8</u> and <u>9</u> in good yield. It should be pointed out that several dienes and dienophiles undergo [4+2]-cycloaddition with the 76[°] dimer of COT to produce products analogous to structures <u>8</u> and <u>9</u>.^{3,10} Finally, the formation of the 1:1-cycloadduct <u>5</u> can be attributed to a ring opening reaction of azomethine imine <u>3</u> followed by a series of hydrogen shifts.

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