## CYCLOADDITIONS OF TROPONE AND DIPHENYLNITRILEIMINE:

A [6+4] 1,3-DIPOLAR CYCLOADDITION

K.N. Houk and Charles R. Watts<sup>\*</sup> Department of Chemistry Louisiana State University Baton Rouge, Louisiana 70803

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The 1,3-dipolar cycloaddition reaction has been the subject of the exhaustive and elegant investigations of Huisgen and co-workers.<sup>1</sup> These reactions show all the characteristics of concerted reactions, including stereospecificity, regioselectivity frequently incompatible with diradical or dipolar intermediates, minimal influence of solvent polarity on rate, moderate activation enthalpies, and large negative activation entropies.<sup>1</sup> Although a recent suggestion has been made that these reactions proceed through diradical intermediates,<sup>2</sup> Huisgen has mounted convincing evidence supporting the concertedness of the majority of 1,3-dipolar cycloaddition reactions.<sup>1b</sup>

Orbital symmetry analysis of 1,3-dipolar cycloaddition reactions has revealed that these reactions are thermally allowed by virtue of the presence in 1,3-dipoles of a  $4\pi$  electron system isoelectronic with the allyl anion.<sup>3</sup> A simple extension of this analysis reveals that 1,3-dipoles may add in a concerted manner to trienes ( $6\pi$ ), but not to dienes ( $4\pi$ ). Armed with this prediction, the study of 1,3-dipolar cycloadditions to trienes was begun, both to seek corroboration of this prediction, and to investigate further the steric, electronic, and spatial factors which induce periselectivity in competing cycloadditions.<sup>4,5</sup>

Diphenylnitrileimine, I, was generated in the presence of tropone by the slow addition of triethylamine to a benzene solution of  $\alpha$ -chlorobenzylidene phenylhydrazine, II<sup>6</sup>, and tropone in

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a lo:1 molar ratio. After 12 hours, filtration of the solution gave a mixture of triethylamine hydrochloride and a light yellow adduct, III. The adduct was freed from the hydrochloride by washing with water and recrystallization from methanol. The pure adduct III, mp  $189-189.5^{07}$  was obtained in 29% yield. A second adduct IV, mp lll-ll3,<sup>8</sup> was isolated in 5% yield by preparative layer chromatography of the original filtrate.



The structure of adduct III was shown by the presence of a conjugated ketone in the ir  $(CCl_4; 6.0l_{\mu})$  and the absence of resonances characteristic of the  $\alpha$  and  $\beta$  protons of  $\alpha,\beta$ unsaturated ketones in the nmr (CDCl\_3: 2.5-3.0 ppm, 2H, m; 6.3-6.5 ppm, 2H, m; 7.2-7.8 ppm, 10H, m). While no evidence has been obtained for the relative orientation of the addends in the adduct, structure IIIa is favored by the observation of similar orientation in the addition of I to ethyl acrylate and ethyl crotonate.<sup>3b</sup> Adduct III is the result of the usual [4+2] 1,3dipolar cycloaddition to the 2,3-double bond of tropone followed by hydrogen shifts, most likely base-catalyzed, to form the aromatic pyrazole nucleus.

The adduct IV proved to be the product of an unprecedented [6+4] 1,3-dipolar cycloaddition to the 2, 7 positions of tropone. The ir spectrum (CCl<sub>4</sub>;  $5.79\mu$ ) and the nmr spectrum (CDCl<sub>3</sub>: 4.5 ppm, dd, J = 7.0, 2.5 Hz, 1 H; 5.08 ppm, dd, J = 5.6, 2.5 Hz, 1 H; AA'BB' pattern 5.98 ppm, 4 H; 7.0-8.0 ppm, 10 H) confirmed the [6+4] nature of this adduct. In particular, the olefinic proton pattern corresponded nearly exactly to those of rigid cyclohexadienes.<sup>9</sup>

Although several additions of 1,3-dipoles to trienes have been reported, the structures of most of the adducts have not been elucidated.<sup>10,11</sup> Only the structures of the adducts of tetracyanoethylene oxide with cycloheptatriene and cyclooctatetraene have been reported, and both of these were shown to be [4+2] 1,3-dipolar adducts.<sup>12</sup>

Although the total yield of adducts isolated in the present case is far from quantitative, the isolation of only thermally allowed adducts is in agreement with studies of 1,3-dipolar additions to dienes,  $^{6,12,13}$  and provides further confirmation of the concerted nature of the 1,3-dipolar cycloaddition. A diradical intermediate as proposed by Firestone could easily collapse to give the [4+4] products in addition to the thermally allowed products.<sup>2</sup>

Studies are in progress to assess the scope of the [6+4] l,3-dipolar cycloaddition and to investigate means of decarbonylation of adducts such as IV to form new  $10\pi$  electron monocyclic heteroaromatic systems.

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