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# REACTION OF 3-AROYLAZIRIDINES WITH DIPHENYLCYCLOPROPENONE. 1,3-DIPOLE CASCADE FROM AZOMETHINE YLIDE TO CARBONYL YLIDE

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*Abstract:* The novel formation of *anhydro*-3-hydroxy-2,4-diphenyl-6-arylpyrylium hydroxide in the reaction of 3aroylaziridines with diphenylcyclopropenones and their 1,3-dipolar cycloaddition reactions with diphenylcyclopropenone, N-phenylmaleimide, dimethyl fumarate, and dimethyl maleate were described.

In 1968, one of the authors reported synthesis and properties of "novel 4-aroyl-4-oxazolines" by reaction of 3-aroylazirizines with diphenylcyclopropenone (DPP).<sup>1</sup> During our studies on cycloadditions of Buckminsterfullerrene, C<sub>60</sub>, with various ylidic compounds,<sup>2, 3</sup> we have chosen the proposed "4-aroyl-4oxazolines" as one of the vlidic candidates because they are highly reactive toward a variety of alkynes and alkenes.<sup>1</sup> However, we have had a doubt concerning the structure and formation of "4-aroyl-4-oxazolines" when we inspected <sup>13</sup>C NMR spectra of "4-aroyl-4-oxazolines".<sup>4</sup> For example, the <sup>13</sup>C NMR spectra of the product 2a from 1-cyclohexyl-2-phenyl-3-benzoylaziridine 1a (a mixture of cis- and trans-isomer) and DPP exhibited a signal at  $\delta$  67.91 due to sp<sup>3</sup> CH carbon and two signals at  $\delta$  88.50 and 97.43 due to quaternary sp<sup>3</sup> carbons. Furthermore, the <sup>13</sup>C NMR spectra of the product **3a** from **2a** and DPP showed two signals at 8 90.01 and 95.65 due to quaternary sp3 carbons. Therefore, we convinced that neither "4-aroyl-4-oxazolines" nor "3-aroylfuran" is correct in structure in the present case. Thus, we decided to perform an X-ray analysis of these products 2a and 3a. Although, in our hands, the compounds 2 were not stable enough towards an X-ray crystal measurement, the adduct obtained from "4-toluoyl-4-oxazoline" formed crystals suitable for an X-ray analysis. An analysis of this adduct established that the compound had structure 3b as shown in Fig. 1.5 This structure immediately has led us that the reactive species is a carbonyl ylide 4 (anhydro-3-hydroxy-2,4-diphenyl-6-arylpyrylium hydroxide), therefore "4-aroyl-4-oxazolines" being the adduct 2 in agreement with <sup>1</sup>H and <sup>13</sup>C NMR spectra. Indeed, there are precedents for this type of carbonyl ylides.<sup>6</sup> The novel formation of the carbonyl ylide 4 can be explained as described in Scheme 1. Little examples are known for the conversion of one dipole into another, though the interconversion of one dipole into another are reported.9

Further 1,3-dipolar cycloadditions of 2 with such typical dipolarophiles as N-phenylmaleimide, dimethyl





Scheme 1



Fig. 1 ORTEP drawing of the compound 3b

maleate, and dimethyl fumarate smoothly took place to afford the corresponding adducts 5, 6, and 7 in 83, 52, and 70% yields, respectively. The stereochemistry of these adducts were unambiguously determined based upon their X-ray analyses. Interestingly, exclusive exo additions were observed in 5.

Theoretical studies to explain these stereoselectivities based on molecular orbital calculations are under way.



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- 3. This aspect will be reported elsewhere in due course.
- 4. No <sup>13</sup>C NMR spectra were available in ref. 1.
- 5. Crystal data of 3b: C38H28N4O2, M=516.64, monoclinic, space group P 2<sub>1</sub>/n (#14), a=11.04(1), b=17.635(2), c=14.556(2)Å, β=94.31(4)°, V=2825(3)Å<sup>3</sup>, Z=4, Dc=1.214 gcm<sup>-3</sup>, µ=0.68 cm<sup>-1</sup>. The structure solution (direct methods) and refinement (full-matrix least-squares) was performed using the TEXSAN software and based on 1631 observed intensities [F>3.0cr(F)] from 6167 measured data (20<55.0°). Final R and R<sub>W</sub> values were 0.056 and 0.059. The tables of atomic coordinates and of bond lengths and bond angles have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB21EZ, U.K.
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