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In the preceding communication<sup>2)</sup> the cis-trans isomerization of the isomeric allocaimenes I A and I B with a variety of  $\pi$ -acids (EA) has been reported. This may be explained by the equilibration of  $\sigma$ -complexes,

which should correspond to the intermediates in two-step cycloaddition reactions<sup>2)</sup>. Therefore, the addition of dimethyl (DMAD) and diethyl azodicarboxy-late (DEAD) to I A and I B has been studied, since both  $\pi$ -acids isomerize I A, and since the formation of 1,2-diazacyclobutane derivatives could have been evidence for a two-step cycloaddition<sup>3)</sup>.

The exothermic reaction (self heating to  $75^{\circ}\text{C}$ ) of 160 mmol I A and 40 mmol DEAD yields 36 mmol II AE (m.p.  $66-68^{\circ}\text{C}$ ). The recovered excess alloocimene contained IA and IB in a 1:1 ratio. II AM (m.p.  $118-120^{\circ}\text{C}$ ) was obtained by a similar procedure. In the reaction of 51 mmol I B and 13 mmol DEAD (self heating to  $78^{\circ}\text{C}$ ) 11 mmol II BE ( $n_{D}^{20}$  1.485) were formed and purified by short-path distillation ( $140^{\circ}\text{C}$ ; 0.03 Torr). II BM (m.p.  $88-89^{\circ}\text{C}$ ) was produced accordingly.

All compounds reported gave satisfactory elemental analyses and molecular weight determinations; the proposed structures are based on spectral data:

IIA:  $UV_{Max}$  36200 cm<sup>-1</sup>, log  $\epsilon$  4.4;  $NH_{(IR)}$  3220 cm<sup>-1</sup> II AM NMR (in CCl<sub>4</sub>):  $H^4$   $H^5$ ,  $H^6$  3.8  $\tau$  (m);  $-NH \sim 3.8$  (b);  $=CH_2^{10}$  4.84 (bs), 4.88 (bs);  $H^2$  4.82 (q);  $CH_3^{8,9}$  8.21 (s);  $CH_3^{1}$  8.69 (d; J=7Hz);  $-OCH_3$  6.27 (s), 6.32 (s), IIB: no  $UV_{Max}$  to 45500 cm<sup>-1</sup> no  $NH_{(IR)}$ . II BM NMR:  $H^4$ ,  $H^5$ ,  $H^6$  5.1  $\tau$  (m);  $H^2$  5.6 (q);  $CH_3^{8,9,10}$  8.28 (bs);  $CH_3^{1}$  8.69 (d; J=7 Hz);  $-OCH_3$  6.28 (s) 6.38 (s).

The sterical inhibition of the s-cis form of I A explains the strikingly different reactivity of I A and I B. While 1,4-addition is easily brought about from the s-cis form of I B with the azodicarboxylates as well as with maleic anhydride<sup>2)</sup>, the behaviour of I A parallels that of many sterically hindered dienes, which give concerted addition-abstraction reactions with DEAD<sup>4)</sup>. The cisposition of the two CH<sub>3</sub>-groups in I B impedes the addition-abstraction reaction<sup>5)</sup>; therefore, it does not compete with 1,4-addition in this case. There was no evidence for 1,2-addition of the azodicarboxylates to I A and I B. It is interesting to note that the reaction of singlet O<sub>2</sub> with I A and I B produces the same hydroperoxide, whose structure corresponds to that of II A<sup>6)</sup>

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