

IIA: UV_{Max} 36200 cm^{-1} , $\log \epsilon$ 4.4 ; $NH_{(IR)}$ 3220 cm^{-1} II AM NMR (in CCl_4) : H^4
 H^5, H^6 3.8 τ (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^{-1} no $NH_{(IR)}$. II BM NMR: H^4, H^5, H^6 5.1 τ (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 anhydride²⁾, the behaviour of I A parallels that of many sterically hindered dienes, which give concerted addition-abstraction reactions with DEAD⁴⁾. The cis-position of the two CH_3 -groups in I B impedes the addition-abstraction reaction⁵⁾; 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_2 with I A and I B produces the same hydroperoxide, whose structure corresponds to that of II A⁶⁾

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References:

- 1) Present address: Max-Planck-Institut für Kohlenforschung Abteilung Strahlenchemie, Mülheim-Ruhr
- 2) E.Koerner von Gustorf, J.Leitich, Tetrahedron Letters 1968, preceding paper.
- 3) E.Koerner von Gustorf, D.White, B.Kim, J.Leitich, to be published.
- 4) B.T.Gillis, Azo Compounds as Dienophiles, in J.Hamer, 1,4-Cycloaddition Reactions, p. 143. Academic Press, New York 1967, and references therein.
- 5) W.A.Thaler, B.Franzus, J.Orq.Chem. 29, 2226 (1964)
- 6) E.Koerner von Gustorf, F.-W.Grevels, G.O.Schenck, Liebigs Ann.Chem., in press