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HINDERED ROTATION ABOUT N-COOR BONDS IN DIHYDRO-OXADIAZINES FROM AZODICARBOXYLATES AND MONOOLEFINS

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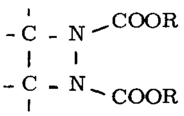
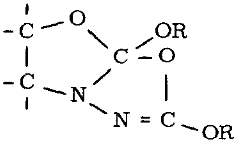
At least 4 different paths are conceivable[3] for cycloaddition reactions of azodicarboxylates with monoolefins:

1.2-Addition[4-6]



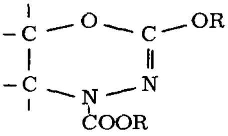
(I)

1.3-Addition[7]



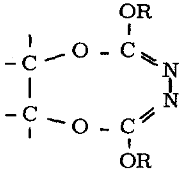
(II)

1.4-Addition[4,8]



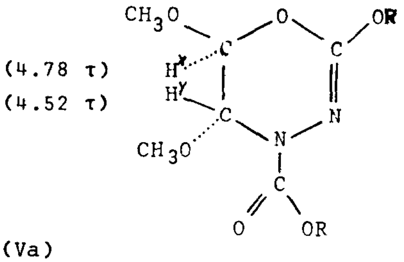
(III)

1.6-Addition[9]

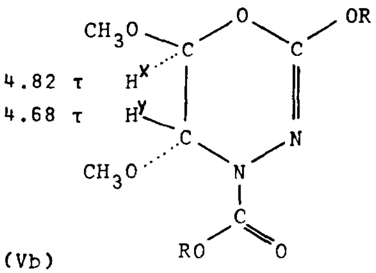


(IV)

If symmetrical 1.2-disubstituted olefins are used (e.g. dioxene, 1.2-dimethoxy-ethylene) the two ring protons are identical in I and IV, but different from each other in II and III. The nmr spectrum (in $CDCl_3$) of the 1:1 adduct (V) of dimethyl azodicarboxylate (DMAD) and trans-1.2-dimethoxy-ethylene shows two doublets for the ring protons at 4.53 and 4.79 τ at 40°C, thus ruling out I and IV. The distinction between II and III rests on the ir data: one should expect one $>$C=N-vibration for II, one $>$C=O and one $>$C=N-vibration for III. V shows three bands in the 1600 - 1800 cm^{-1} region: at 1678, 1714 and 1750 cm^{-1} (in CCl_4); at 1660, 1688 and 1727 cm^{-1} (in KBr). A possible explanation could be a conformational equilibrium Va ⇄ Vb:



(Va)



(Vb)

The inspection of molecular models shows that the overlap of the π-orbital of the CO group with the n-orbital of the nitrogen should be greater in Va than in Vb, due to less steric interaction of OCH_3 with $\gt CO$ than with OR. Therefore two different $\gt C=O$ vibrations (Va at lower wave numbers) could be expected. Hindered rotation about a $\gt N-COOR$ bond can be easily detected by nmr at low temperatures[10)]. At -30°C the nmr spectrum of V shows doubling of the two ring proton doublets. This process is not due to a change of the ring conformation, since the small coupling constant $J_{xy}=1.4$ cps (typical for vicinal H - antiperiplanar to N, O - in equatorial positions)[11)] remains unchanged. N-inversion appears very improbable too, since overlap with the $\gt CO$ group causes a substantial change in hybridization towards sp^2, facilitating this process. Hindered rotation about a $\gt N-COOR$ bond appears to be the most probable process. The free enthalpy of activation ΔG^* at the coalescence temperature T_c (280°K for V) can be calculated with some reservations from the equation[10a)]:

$$\Delta G_c^* = 4.57\ T_c\ (9.97 + \log T_c/\Delta\nu)$$

with $\Delta\nu$ being the separation of the two signals when exchange is slow ($\Delta\nu = 10$ cps for the low field ring proton of V). The value of 14.6 kcal/mol obtained for V is in the region of 13.5 ± 1.5 kcal/mol determined for hindered rotation about $\gt N-COOR$ bonds in various tetrahydropyridazine derivatives[10)].

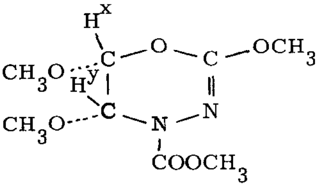
The ratio of the two conformers is 3.5 : 1 at - 30°C according to the integration. The ring protons appear more shielded in the less abundant conformer as expected for Vb. The ratio of intensities [12)] of the vibrations in V at 1714 and 1750 cm^{-1} is 4.5 : 1, lending further support to the assignment of Va and Vb given. ($\gt C=N$ at 1678 cm^{-1}). The spectral data presented for V are incompatible with the structural type II.

DMAD forms 1:1 adducts VI, VII and VIII with cis-1.2-dimethoxy ethylene[4)], dioxene[4)], and indene[4, 13)]. All these adducts show ir data similar to those of V, and the low temperature nmr spectra (in $CDCl_3$) reveal a conformational process, too.

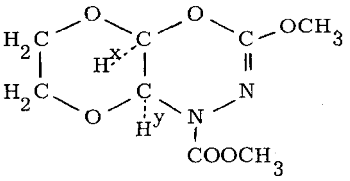
Adduct	Temp.	H^y [τ]	H^x [τ]	J_{xy} [cps]	T_c	Δ G* [kcal/mol]
VI	40°C	4.42(d)	4.84(d)	1.8		
	-20°C	4.37 (d) ?)	4.81(d) ?)		< 0°C	
VII	40°C	4.39(d)	4.59(d)	1.6	-20°C	13.2
	- 40°C	4.35(d) 4.52	4.59(d)	1.6		
VIII	40°C	4.65(d)	5.06(o)	5	-30°C	13.3
	- 54°C	4.48(d) 4.52(d)	~ 4.9 (m)	5		

d = doublet, o = octet, m = multiplet, ?) = position uncertain

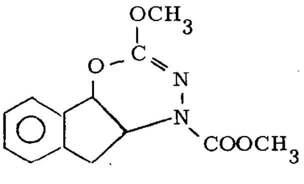
This conformational process in VI-VIII appears to be due to hindered rotation about a >N-COOR bond as in V. Therefore, dihydro-oxadiazine structures should be assigned to VI - VIII .



(VI)



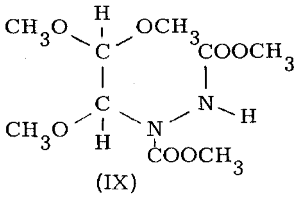
(VII)



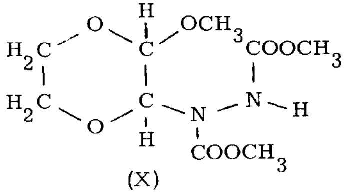
(VIII)

Compounds V - VII add 1 mol CH_3OH/mol, simply by being dissolved in CH_3OH (and excess solvent being stripped off). V and VI yield the same adduct IX with CH_3OH; however, diastereomeric adducts IXa and IXb are obtained with CD_3OD, demonstrating the S_N2 character of this reaction.

The ir spectra (in CCl_4) show NH (3400 cm^{-1}), C=O (1765, 1730 cm^{-1}), amide-II (1485 cm^{-1}) and no >C=N-, thus supporting the assigned structures14). X, the adduct of CH_3OH + VII, shows the ring protons in diaxial positions according to the relatively large J_{xy}.



(IX)



(X)

Compound	Solvent	H^y [τ]	H^x [τ]	J_{xy} [cps]	$O{=}\overset{|}{C}{-}OCH_3$ [τ]	$-\overset{|}{\underset{|}{C}}-OCH_3$ [τ]
IX	$CDCl_3$	4.78	5.69	6.5	6.19, 6.23	6.48, 6.55, 6.65
IXa	CD_3OD	4.87	5.69	6.5	6.22, 6.27	6.54, 6.65
IXb	$CDCl_3$	4.79	5.58	6.5	6.19, 6.23	6.48, 6.54
X	$CDCl_3$	4.88	5.54	6.5	6.19	6.50

A conformational process [resulting in doubling of the H^y doublet] is detected in IX by nmr at 10°C. $\Delta G^* = 14.4$ kcal/mol for this process is in good agreement with the values obtained for hindered rotation about >N-COOR bonds in the dihydro-oxadiazines.

The technical assistence of Miss I. Gerlach in measuring the nmr spectra is gratefully appreciated.

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2) Doctoral Dissertation, Boston College, 1969

3) See lit4) for detailed discussion

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    (b.) 24, 137 (1968)

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12) Assuming equal extinction coefficients

13) C. F. Huebner, E. M. Donoghue, C. J. Novak, L. Dorfman, and E. Wenkert, J. Org. Chem., in press. Helpful correspondence with Dr. Huebner prior to publication is gratefully acknowledged.

14) All new compounds gave satisfactory elemental analyses and mass spectra.