

ALKANOYLNITRENES : STABILIZATION OF THE SINGLET STATE BY DICHLOROMETHANE.

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One source of solvent effects to be expected in nitrene chemistry is solvent interaction speeding up or slowing down the intersystem crossing of nitrenes. This will change the singlet to triplet ratio in cases where intersystem crossing competes with chemical reactions, and the ratio of singlet products to triplet derived products will change. Acceleration of singlet to triplet crossing by heavy atom solvents has been reported for cyanonitrene (1). Deceleration of singlet - triplet crossing may be expected in solvents providing suitable overlap with unshared electron pairs (2). Dichloromethane might be expected to be a singlet stabilizing solvent, but no significant differences in yields and product ratios were found in our studies of ethoxycarbonylnitrenes when we compared dichloromethane and hydrocarbons as the solvents (3).

We now report large solvent effects in reactions of alkanoylnitrenes, R-CO-N. Using dichloromethane instead of hydrocarbons as the solvent drastically affects both intra- and intermolecular reactions. Table I shows the total yields of C-H insertion products obtained from photolyses of a number of alkanoyl azides in dichloromethane and in cyclohexane solutions. In the absence of solvent effects, the total insertion yields should be higher in cyclohexane solution, because the nitrenes have a greater chance to interact with a suitable C-H bond before undergoing competing processes (such as dissociation or intersystem crossing) (4, 5). The opposite is observed : In dichloromethane solution the C-H insertion yields are almost twice as high as in cyclohexane, despite the fact that only the stereochemically unfavorable cyclization route is open to the nitrene (insertion into C-H bonds of dichloromethane is not observed). Only the 2,2,3,3-tetramethylbutanoylnitrene shows no solvent effect : It cyclizes quantitatively in either solvent, no doubt because a double geminal dimethyl effect curls up the molecule in a conformation which situates a suitable C-H bond right on top of the developing nitrene. The yields given in Table I are based on starting azide. Only about 60% of the azide is converted to nitrene, the other 40% undergoes concerted photo-Curtius rearrangement to the corresponding isocyanate (6). To base the yields on nitrene, one has to multiply them by approximately 1.7. In the cyclization process, about twice as much δ -lactam as γ -lactam is formed, a fact observed earlier by Edwards (7) and readily understood for stereochemical reasons on the basis of a concerted insertion mechanism (5) involving the singlet nitrene and a three-membered cyclic transition state (7). The data in Table I can be understood by assuming that the dichloromethane stabilizes the insertion-active state of the nitrenes (the singlet (5)) without removing its C-H insertion reactivity.

Table I : Photolysis of some Alkanoyl Azides in Dichloromethane and in Cyclohexane

A z i d e	Solvent	Yields in % based on Azide			Total
		Intramolecular Products γ -Lactam	Insertion δ -Lactam	N-Cyclohexyl- alkanoylami- de	
C ₄ H ₉ -CO-N ₃	CH ₂ Cl ₂	23.5	not obsd.		23.5
	C ₆ H ₁₂	7.8	"	4.7	12.5
Me ₃ C-CH ₂ -CO-N ₃	CH ₂ Cl ₂	20.1	"		20.1
	C ₆ H ₁₂	5.4	"	8.2	13.6
H ₅ C ₂ -CMe ₂ -CO-N ₃	CH ₂ Cl ₂	36.5	"		36.5
	C ₆ H ₁₂	11.2	"	7.4	18.6
Me ₃ C-CMe ₂ -CO-N ₃	CH ₂ Cl ₂	56.2	"		56.2
	C ₆ H ₁₂	58.3	"	0	58.3
n-C ₅ H ₁₁ -CO-N ₃	CH ₂ Cl ₂	10.8	22.7		33.5
	C ₆ H ₁₂	5.1	11.7	1.9	18.7
n-C ₇ H ₁₅ -CO-N ₃	CH ₂ Cl ₂	11.0	21.0		33.0
	C ₆ H ₁₂	5.5	11.5	1.4	17.4

When pivaloyl azide is photolyzed at -15° in the presence of olefins, the corresponding N-pivaloylaziridines are formed, together with a constant yield (about 40%) of the Curtius rearrangement product, tBuNCO (cf. 6). Neopentane and even cyclopentane can be used as solvents, because the olefin competes effectively for the nitrene. In dichloromethane solution, trans 2-butene forms trans 1-pivaloyl-2,3-dimethylaziridine in a yield almost independent of olefin concentration over a range from 2 to 50 mole%. In cyclopentane solution, the aziridine yield drops drastically with decreasing olefin concentration, although the volatile products include little or no N-cyclopentylpivalamide (Table II). At olefin concentrations of 10 mole% and less (in cyclopentane but not in dichloromethane), a host of new volatile products appears, presumably formed from the dissociation products of pivaloylnitrene, isobutene and cyanic acid (4).

Photolysis of pivaloyl azide in dichloromethane - trans 4-methyl-2-pentene mixtures gave (cf. 8) stereospecifically the trans aziridine as the main product. This trans aziridine is thermodynamically less stable than its cis isomer because both N-invertomers experience pivaloyl-alkyl interaction. The trans aziridine yield increases markedly with decreasing olefin concentration (Table III). Similar results were obtained using other olefins (cis 4-methyl-2-pentene and cis 2-butene) and other hydrocarbon solvents (neopentane). For ethoxycarbonylnitrene, we have shown that it is the singlet state which effects C-H insertion (5) and stereospecific addition to double bonds (8). It seems reasonable to assume that this also applies to the alkanoylnitrenes, and our results are simply explained by concluding that solvation by CH₂Cl₂ stabilizes the singlet state of our alkanoylnitrenes while hydrocarbons do not - just as expected.

Table II : Photolysis of Pivaloyl Azide in trans 2-Butene Solutions

Olefin Conc. mole%	Yield of <u>trans</u> Adducts (% , based on azide)	
	In CH ₂ Cl ₂	In Cyclopentane
50	30.8	20.5
20	32.0	18.8
15	-	16.4
10	31.1	9.5
5	33.8	not measurable
2	29.3	not measurable

Table III : Photolysis of Pivaloyl Azide
in Dichloromethane Solutions of trans 4-Methyl-2-pentene

Olefin Conc. mole%	Yield of <u>trans</u> Aziridine
	(based on azide) %
78	7.4
68	7.7
57	11.0
47	12.9
23	16.2
9	18.5
3	20.5
1.3	16.3

The singlet state of ethoxycarbonylnitrene, EtO-CO-N, seems not to be noticeably stabilized by dichloromethane, indicating that intramolecular interaction of the ether oxygen with the nitrene nitrogen competes effectively with the "proper" dichloromethane solvation: Hoffmann's calculations (2) demand symmetrical interaction of two unshared electron pairs with the nitrene if singlet stabilization is to be achieved. However, hexafluorobenzene seems to compete more favorably (or interaction of the ether oxygen lone pair and one fluorine lone pair is more suitable), because D. S. Breslow (9) observes singlet stabilization of ethoxycarbonylnitrene by hexafluorobenzene. Substantial interaction of the ether oxygen with the nitrogen in ethoxycarbonylnitrene agrees with earlier spectroscopic data (10).

In view of the large concentrations of dichloromethane required to produce noticeable stabilization, our effect seems to be different from the effect of small concentrations of radical traps, observed by D.S. Breslow (11) to increase the yields of singlet products.

Details on the addition of pivaloylnitrene to olefins (12) will be reported elsewhere.

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