

**Dilution Effects on the Reaction of Carbethoxynitrene with
trans-1,2-Dimethylcyclohexane with Hexafluorobenzene
and Reactive Solvents**

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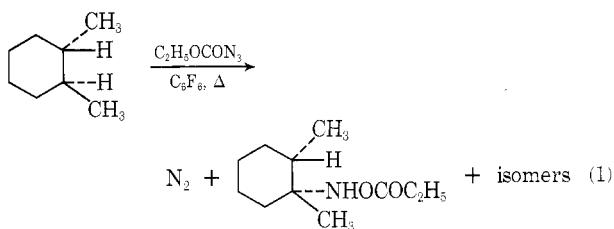
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Absolute yields, stereospecificity, and selectivity of reaction are reported for the thermal decomposition of ethyl azidoformate in *trans*-1,2-dimethylcyclohexane using hexafluorobenzene as an inert diluent. Hexafluorobenzene is shown to have a stabilizing interaction on the singlet state of the resulting carbethoxynitrene as manifested by increased absolute yields with increasing dilution. Comparisons are made with previous results using dichloromethane to illustrate the generality of this theoretically predicted singlet stabilization. The absolute yield but not the selectivity or stereospecificity is shown to be very dependent on azide molarity (extent of dilution) even without inert, singlet-stabilizing solvents present.

In a previous communication, we reported on the ability of dichloromethane to stabilize the singlet state of carbethoxynitrene as manifested by an increase in absolute yield of insertion products with *trans*-1,2-dimethylcyclohexane upon dilution with dichloromethane and a reduction in the selectivity (tertiary-secondary-primary insertion products) of the reaction with dilution as progressively more of the nitrene exists as a nitrene-solvent complex.¹ A similar reduction of selectivity in the presence of halogenated solvents has been recently reported by Tardella et al., based on a study of the insertion reaction of carbethoxynitrene with bicyclo[4.0.0]alkanes.²

An increase in absolute yield for the insertion reaction of carbalkoxynitrenes with hydrocarbons upon dilution with hexafluorobenzene has also been observed.³ Hexafluorobenzene is an inert solvent which has the symmetrical lone pairs of electrons necessary for stabilization of singlet nitrenes according to the proposal of Gleiter and Hoffmann.⁴ Since insertion yields from the singlet nitrene have been observed to increase in the presence of radical (triplet nitrene) traps,⁵ some question has existed whether the effect of C₆F₆ is that of singlet stabilizing by complex formation as with CH₂Cl₂ or whether it is functioning as a radical trap. A related question arising from the use of CH₂Cl₂ and C₆F₆ as solvents is whether the singlet stabilizing phenomenon is limited to the reactions of alkanoylnitrenes (ROCN) or includes carbalkoxynitrenes (ROCON) as well.^{6,7} In the first part of this paper, we will report our results of a study of the effect on stereochemistry, selectivity, and absolute yield of dilution with hexafluorobenzene of the reaction between thermally generated carbethoxynitrene and *trans*-1,2-dimethylcyclohexane (eq 1). The re-



sults in Table I are based on triplicate runs with an error of $\pm 1.0\%$ for the stereospecificity, $\pm 1.0\%$ for the selectivity (percent tertiary), and $\pm 2.0\%$ for the absolute yield. The data in Table I which deal with the effect of dilution on absolute yields are presented in graphical form in Figure 1. The absolute yield of C-H insertion products is shown to increase dramatically upon initial dilution of the azide-hydrocarbon reaction mixture with C₆F₆ with an eventual

Table I
Thermal Decomposition of Ethyl Azidoformate in
Hexafluorobenzene-*trans*-1,2-Dimethylcyclohexane
(TDCH) Solutions^a

Concn TDCH, mol % ^b	Azido- formate, M	Stereospecificity (%)		Selectivity (% tertiary product) ^c	Absolute yield, % ^d
		trans product)	insertion product)		
100.0	0.660	96.9	40.6	26.0	
89.2	0.602	97.0	41.4	33.3	
74.7	0.510	98.2	40.1	41.2	
50.1	0.344	96.9	36.3	42.7	
25.0	0.170	95.3	36.2	44.2	
10.7	0.078	90.9	35.1	44.8	

^a Reaction mixtures were carefully degassed and azide decomposition was carried out in evacuated, sealed tubes at 120° for 90 hr; analysis by BPC. ^b The mol % TDCH is computed from the number of moles of TDCH and C₆F₆ present and does not include the azidoformate concentration. ^c Percent tertiary C-H insertion product of other isomers combined: (tertiary)/(tertiary + secondary + primary) × 100. ^d Total absolute yield of all insertion isomers.

leveling off at high dilution. The range of absolute yields agrees with our previous results¹ using CH₂Cl₂ as the diluent, although C₆F₆ shows a smooth increasing trend and a higher final absolute yield whereas CH₂Cl₂ showed an initial increase with no noticeable trend thereafter.

Based on our selectivity data, we conclude that CH₂Cl₂ forms a stronger complex with carbethoxynitrene than C₆F₆, since at high dilution the percent tertiary product is substantially less with CH₂Cl₂ as solvent than with C₆F₆. The stereospecificity data is in accord with many observations that only the singlet carbethoxynitrene (complexed or not) inserts into inactivated C-H bonds.⁸ It is noteworthy that at the highest dilution with both CH₂Cl₂ and C₆F₆, the stereospecificity is somewhat lower than for the other concentrations whereas with TDCH (a reactive diluent) Table II shows no decrease at high dilution. It is conceivable that at very high dilution with inert solvent, collisional deactivation of singlet to triplet nitrene begins to compete with singlet insertion or complex formation. There is evidence for some radical character (CH₃CH₂OCO⁺NH formed from the triplet nitrene) in thermal reactions of ethyl azidoformate with hydrocarbons and this could be responsible for a small amount of nonstereospecifically formed insertion product or for *cis*-*trans* isomerization of the tertiary insertion product.⁹ If the small decrease in stereospecificity were due to partial radical character, then this would be evidence against C₆F₆ acting as a radical trap in these reac-

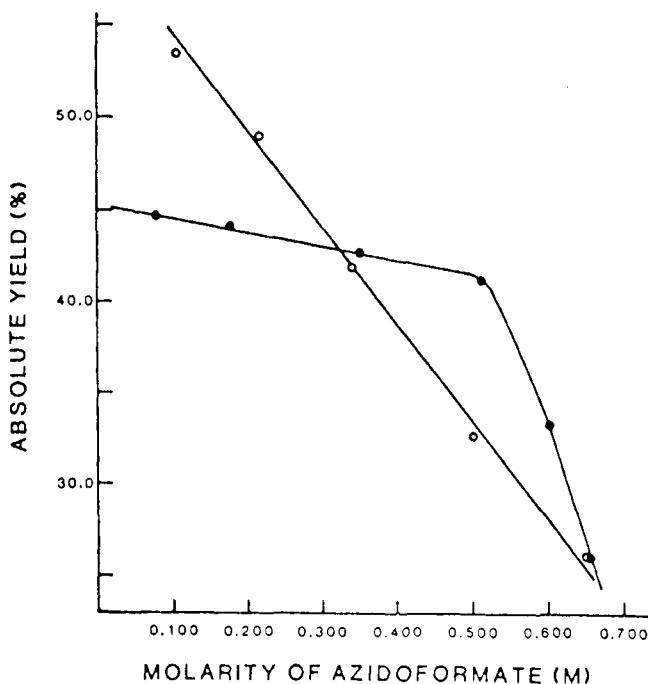


Figure 1. Absolute yield of TDCH insertion products as a function of azidoformate molarity: ●, dilution with C_6F_6 ; ○, dilution with TDCH.

tions, since the stereospecificity should remain high or should increase with increasing dilution with C_6F_6 . Moreover, the hexafluorobenzene even for the initial dilution experiment (89.2 mol % TDCH and 10.8 mol % C_6F_6) is present in much greater concentration than the azidoformate. Therefore, although the initial increase in absolute yield might be explained by C_6F_6 acting as a radical trap, the steady increase in yield with subsequent dilution is not explicable on this basis.

In these studies the weight ratio of azidoformate to hydrocarbon was kept the same at about 1:10. This is an excess of hydrocarbon similar to that employed by Lwowski in his studies of dichloromethane dilution effects on the reaction of ethyl azidoformate with 3-methylhexane¹⁰ to which our results were compared. Suitable volumes of CH_2Cl_2 or C_6F_6 are then added to give solutions of lower mole percent TDCH and lower molarity of azidoformate. Although the absolute yields we presented in our previous paper¹ and in Table I agreed with those of Lwowski,¹⁰ these yields are low (25–45%) compared to those obtained by other workers studying carbalkoxynitrene-saturated hydrocarbon reactions, e.g., Breslow (50–75%).³

Table II presents the results of a series of experiments designed to test the assumption that a 10:1 ratio of hydrocarbon to azide constitutes a sufficiently great excess of hydrocarbon to ensure reaction between the nitrene and hydrocarbon uncomplicated by yield-reducing side reactions. Figure 1 shows the dependence of absolute yield of insertion products of TDCH on the molarity of the azidoformate with TDCH itself as the diluent. It is evident that a hydrocarbon-azide ratio of 10:1 (approximately 0.66 M) is not a sufficiently great excess of hydrocarbon to ensure maximum yields of insertion products. However, the absolute yield appears to be the only result which is noticeably affected by dilution with the reacting hydrocarbon itself; the selectivity and stereochemistry remain about the same through the dilution range. Figure 1 shows that dilution with hexafluorobenzene causes a considerably greater initial increase in absolute yield than does dilution with the reacting hydrocarbon itself.

The decrease in absolute yield of insertion products with

Table II
Thermal Decomposition of Ethyl Azidoformate in
trans-1,2-Dimethylcyclohexane^a

Azidoformate, M	Stereospecificity (% trans insertion product)	Selectivity (% tertiary product)	Absolute yield, %
0.665	96.9	40.6	26.0
0.501	97.5	39.7	32.4
0.341	99.1	39.9	41.8
0.228	97.8	39.0	49.0
0.100	98.2	37.0	53.8

^a See Table I for definition of terms and reaction conditions.

increasing molarity of the azidoformate in the saturated hydrocarbon (Table II) is not compensated for by an increase in yield of the ethyl carbamate (triplet abstraction) product. In our study, the ethyl carbamate (urethane) yield decreased slightly as the molarity of azidoformate increased and in another study¹⁰ involving thermolysis of ethyl azidoformate in saturated hydrocarbon solutions the insertion yields but not the ethyl carbamate yields were changed by dilution experiment.

Ethyl azidoformate was thermally decomposed in solutions (approximately 0.6 M) of dichloromethane and of carbon tetrachloride under conditions exactly the same as those employed to obtain the data in Tables I and II. For both solvents gas chromatographic analysis showed only solvent, a small amount of unreacted azide, and a trace amount of urethane. Slightly more urethane was observed using CH_2Cl_2 as inert solvent. Some polymeric material was deposited in the tubes and the solutions were light yellow after reaction using either solvent.

The conclusion based on the evidence accumulated in these and other experiments is that the side reaction responsible for reducing the insertion yields is the decomposition of the nitrene itself.

Experimental Section

The general reaction procedure for these sealed-tube reactions and the analysis and characterization of the insertion products have been previously described.¹ It was subsequently determined that reaction times as short as 48 hr are sufficient to ensure complete decomposition of the azide without changing the yield, stereospecificity, or selectivity.

The source and purity of the ethyl azidoformate, dichloromethane, and *trans*-1,2-dimethylcyclohexane reagents has also been given in a previous work.¹

Hexafluorobenzene (Aldrich) was found to be >99% pure by VPC analysis and was used without further purification.

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Registry No.—*trans*-1,2-Dimethylcyclohexane, 6876-23-9; hexafluorobenzene, 392-56-3; ethyl azidoformate, 817-87-8.

References and Notes

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