Tetrahedron Letters No. 20, pp 2041 - 2044, 1972. Pergamon Press. Printed in Great Britain.

THE EFFECT OF HEXAFLUOROBENZENE ON CARBOALKOXYNITRENE REACTIONS*

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(Received in USA 14 February 1972; received in UK for publication 11 April 1972)

Since hexafluorobenzene has been reported to be inert to carbene reactions (1), we considered it of interest to investigate it as a potentially inert diluent in a study of the thermolysis of azidoformates in cyclohexane. In the normal course of events, dilution with an inert solvent should result in the initially formed singlet nitrene undergoing an increased amount of intersystem crossing to the ground state triplet (2). Since the evidence is overwhelming that insertion of a carboalkoxynitrene into the C-H bond of a saturated hydrocarbon is a singlet reaction (2), dilution with C_6F_6 should lead to a decreased yield of substituted carbamate. Surprisingly, the reverse was found with several azidoformates.

Thus, a solution of ethyl azidoformate in cyclohexane was heated overnight at 120° in a capped polymerization tube; 48% HBr and a weighed amount of n-hexylamine internal standard were added, and the mixture was stirred and heated at 130° for 22 hrs. After cooling, the aqueous layer was separated and evaporated to dryness, the solid residue was dissolved in methanol, the solution was made strongly alkaline with methanolic KOH and analyzed for cyclohexylamine by v.p.c.

$$C_2H_5OCON_3 \xrightarrow[-N_2]{\Delta} \left[C_2H_5OCO\underset{\cdot\cdot}{\ddot{N}} \right] \xrightarrow{C_6H_{12}}$$

$$C_2H_5OCONHC_6H_{11} \xrightarrow[2.\ KOH]{1.\ aq.\ HBr} C_6H_{11}NH_2$$

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*Hercules Research Center Contribution No. 1590

In two experiments the yields of cyclohexylamine were 51 and 54%, in excellent agreement with the 52 ±3% reported by v.p.c. analysis for cyclohexylurethan (3). Dilution of the cyclohexane with an equal volume of hexafluorobenzene raised the insertion yield to 75-76%. Similarly, oxydiethyl bis(azidoformate), $O(CH_2CH_2OCON_3)_2$, gave a 40% yield of cyclohexylamine in cyclohexane and a 67% yield in 1:1 C_6H_{12}-C_6F_6.

In Table I is shown the effect of hexafluorobenzene concentration on the insertion of n-octadecyl azidoformate into cyclohexane. Why the insertion yield in this case peaks at a lower C_6F_6 concentration is not obvious. It is quite apparent, from the high insertion yields, that C_6F_6 does not seriously interfere with the insertion of singlet nitrene into a C-H bond; the decreased yield on dilution can be attributed to intersystem crossing, since triplet carbethoxynitrene has been demonstrated not to

Table I

Reaction of n-$C_{18}H_{37}OCON_3$ With Cyclohexane in the Presence of C_6F_6

Cyclohexane, Vol. %	Insertion Yield, %
100	55, 54
90	67
75	63
50	54
25	33

insert into hydrocarbon C-H bonds (2).

There are several possible explanations for this unusual result. Hexafluorobenzene could be acting as a radical trap. There have been several reports of free-radical addition to C_6F_6 (4-6), and Schuster (7) has recently postulated the reversible addition of triplet benzophenone to hexafluorobenzene. Actually the insertion yields are not too different from those obtained by diluting cyclohexane with tetrachloroethylene or by the addition of small quantities of known traps (3). In agreement with this hypothesis, the yield of abstraction product, $ROCONH_2$, which is assumed to arise from triplet nitrene, decreased from 25% to 12% (R = Et) upon the addition of 10% C_6F_6.

Alternatively, the singlet nitrene might complex with the fluorine in C_6F_6 to give a nitrenoid-type species which is stable enough to decrease the rate of intersystem crossing but active enough to insert into the C-H bond of a saturated hydrocarbon. Methylene chloride does not appear to have the same effect (2). It does, however, increase the singlet reactivity of several alkanoylnitrenes (8), suggesting that the nitrene-halide complex hypothesis is the more likely one.

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