starting material and 2-propylphenyl acetate, respectively, by comparison of the ir and nmr spectra with those of authentic samples. The fourth compound (18%) was not identified. The third compound (22%) was identified as 2-(1-propenyl)phenyl acetate (3): ir (neat) 5.75 (-OAc), 6.1 μ (C=C); nmr (CDCl$_3$) δ 1.89 (d, 3 H, CH$_3$C=C-), 2.32 (s, 3 H, CH$_3$COO-), 6.3 (m, 2 H, -CH=CH-), and 7.25 (m, 4 H, aromatic).

When the above run was repeated using 7.7 g (0.077 mol) of concentrated H$_2$SO$_4$, only 2-propylphenyl acetate (70%) was isolated.

Aromatization of 2-butylcyclohexanone gave similar results (Table I).

Reaction of Hydrogen Chloride with Methylcyclohexanones. Into three separate test tubes were charged 5 ml each of cyclohexanone and 2-methyl- and 4-methylcyclohexanone. Hydrogen chloride was bubbled at room temperature into each of the test tubes for 15 min. Analysis of the products by ir and nmr indicated that cyclohexanone and 4-methylcyclohexanone gave different products than the starting material whereas 2-methylcyclohexanone was recovered unreacted.

Registry No.—1a, 583-60-8; 1b, 4423-94-3; 1c, 94-65-5; 1d, 1126-18-7; 1e, 90-42-6; 3 acetate, 35922-87-3; cyclohexanone, 108-94-1; 4-methylcyclohexanone, 589-92-4; hydrogen chloride, 7647-01-0.

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Effect of Dichloromethane on the Reaction of Carbethoxynitrene with *trans*-1,2-Dimethylcyclohexane

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There is ample experimental evidence to support the statement that nitrenes, generated from a variety of precursors, can be made to cross from an initially formed singlet state to a lower energy triplet state by collisional deactivation with inert solvent molecules.¹⁻³ Collisional deactivation or destabilization of singlet states by inert solvents can mean the actual promotion of intersystem crossing by electronic interactions as with heavy-atom solvents or, as is more probably the case with dichloromethane, simply that the solvent by being inert allows intra-

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

Mol % TDCH	Stereospecificity (% trans insertion product)	Proportion of tertiary product^b	Absolute yield %^{c}
100	96.5	38.7	26.2
89.9	98.5	39.6	37.3
79.9	97.8	35.6	34.4
66.7	96.2	38.1	30.0
51.0	94.5	35.4	38.0
39.5	95.6	33.7	37.5
19.2	96.4	28.2	35.2
8.1	92.0	22.6	37.7

^{a} Reaction mixtures were carefully degassed and azide decomposition was carried out in evacuated, sealed tubes at 120° for 90 hr; analysis by vpc. ^{b} Proportion of tertiary C–H insertion product to other isomers; tertiary/(tertiary + secondary + primary). ^{c} Total absolute yield of all insertion products.

molecular intersystem crossing to compete favorably with reactive collision, or both.

However, Breslow has recently reported that yields of insertion (singlet) products of carbalkoxynitrenes, ROCON, with cyclohexane are increased upon dilution with hexafluorobenzene.⁴ Furthermore, in an accompanying communication, Lwowski demonstrates that dichloromethane acts to stabilize the singlet-state character of a number of alkanoylnitrenes, RCON, without removing their C–H insertion reactivity,⁵ although it was noted that no such effect of dichloromethane on yields and product ratios had been observed from previous studies with carbethoxynitrene, ROCON, R = Et.⁶

As part of a long-range study of the factors which influence the singlet–triplet character of nitrenes, we now present evidence that dichloromethane has a noticeable effect on the reactions of a carbalkoxynitrene (ROCON) as well as alkanoylnitrenes (RCON). Table I summarizes results from a study of the reaction of thermally generated carbethoxynitrene with *trans*-1,2-dimethylcyclohexane (TDCH) at various dilutions with dichloromethane (eq 1).
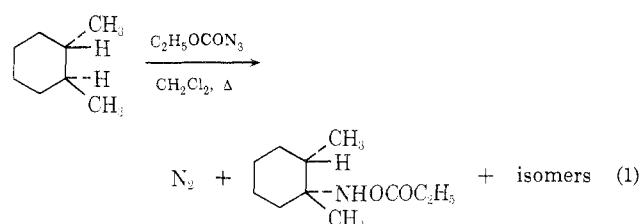
The results given for each concentration of hydrocarbon are based on triplicate runs with an error of ±2% for the stereospecificity, ±2% for the proportion tertiary product, and ±5% for the absolute yields. From the data in Table I it is evident that changing the concentration of the hydrocarbon by dilution with dichloromethane does not affect the stereospecificity of the insertion; *i.e.*, little *cis*-1,2-dimethyl-1-cyclohexylurethane is formed from the trans hydrocarbon. This result supports the conclusion, based on a wealth of other experiments, that only singlet carbethoxynitrene inserts into unactivated C–H bonds.⁷ Competition experiments established that the tertiary C–H bonds of *cis*-1,2-dimethylcyclohexane react 1.2 times faster than the corresponding bonds in the trans isomer; a factor of 1.7 was found for these hydrocarbons using cyanonitrene, NCN.² Otherwise, the cis and trans isomers gave similar product patterns on vpc analysis and the trans isomer was chosen for study. With pure (>99%)

trans hydrocarbon, the selectivity (corrected for numbers of hydrogens) for tertiary:secondary:primary C–H bonds was found to be 34:14:1, in good agreement with previous results.[8] However, Table I shows a steady decrease in the selectivity of the insertion, *i.e.*, the proportion of tertiary insertion product decreases with increasing dilution with dichloromethane. This contrasts with previous experiments in which no change in selectivity upon dilution with dichloromethane was observed for the thermal or photochemical decomposition of ethyl azidoformate in 3-methylhexane[9] nor for the reaction of 2-methylbutane with carbethoxynitrene generated by photolysis or α-elimination.[10] The absolute yields in Table I show an initial increase followed by no evident increase or decrease down to a dilution of 8% hydrocarbon–92% dichloromethane. Breslow also observed an increase of insertion yield for the thermal decomposition of *n*-octadecyl azidoformate in cyclohexane upon dilution with hexafluorobenzene (at concentrations of 90, 75, and 50% hydrocarbon) and only when the concentration of hydrocarbon was reduced to 25% by dilution was the insertion yield lower than for 100% hydrocarbon.[4] An increase in insertion yield was also observed upon 50:50 dilution with hexafluorobenzene of a thermal decomposition reaction of ethyl azidoformate in cyclohexane.[4] However, yields of insertion products only decreased when dichloromethane was used to dilute reactions involving carbethoxynitrene generated from ethyl azidoformate with 3-methylhexane[9] and cyclohexene.[6]

Discussion

Stabilization of nitrene singlet states by symmetrical interaction with two lone pairs has been proposed by Gleiter and Hoffmann[11] and such an effect has been invoked to explain the singlet stabilizing effect of hexafluorobenzene on carbethoxynitrenes[4] and of dichloromethane on alkanoylnitrenes.[5] A possible theoretical explanation of why dichloromethane seems to stabilize the singlet state of alkanoylnitrenes (RCON) but not (previous to our results) of carbalkoxynitrenes (ROCON) has been recently provided.[12] Based on LCAO–MO–SCF calculations, Alewood, *et al.*, concluded that singlet–triplet separations in carbalkoxynitrenes may be much smaller than for alkanoylnitrenes and that this may manifest itself in a reduced tendency of carbalkoxynitrenes to undergo intersystem crossing. Then, to explain the effect of hexafluorobenzene on carbalkoxynitrenes, these authors[12] point out that Breslow and Edwards[4] suggest the possibility that C₆F₆ might be acting as a radical (triplet) trap. Although Breslow and Edwards do discuss the radical-trap hypothesis, they finally concluded that the nitrene–halide complex hypothesis is the more likely one,[4] *i.e.*, C₆F₆ stabilizes singlet carbalkoxynitrenes by the same type of interaction[11] by which CH₂Cl₂ stabilizes singlet alkanoylnitrenes.

Based on the data in Table I, we conclude that dichloromethane has a singlet stabilizing effect on carbalkoxynitrenes as well as on alkanoylnitrenes. The singlet character of the insertion reaction of carbethoxynitrene, as determined by the stereospecificity, remains high throughout the range of dilution. The absolute yields also remain unchanged, after an initial increase similar to that observed in the hexafluorobenzene–carbethoxynitrene system. The lack of any trend of increasing or decreasing absolute yields with successive dilution is probably the result of a counterbalancing of the normally observed collisional deactivation (singlet destabilizing) effect of an inert solvent and the singlet stabilizing ability of this particular inert solvent, dichloromethane. That such an initial increase of insertion yield or the maintenance of high insertion yields upon dilution with dichloromethane of carbethoxynitrene–hydrocarbon reaction mixtures was not previously observed is probably due to the fact that there were no data presented in the region of 33–100 mol % hydrocarbon; *i.e.*, data are presented for 100 mol % hydrocarbon and then typically for dilutions of 33 or 25% hydrocarbon and less but none inbetween.[1,6,9,10,13] The effect of increased yield is observed at 50, 75, and 90% hydrocarbon with hexafluorobenzene[4] and at 90% and other concentrations in this work.

To support the statement that dichloromethane has no significant effect on insertion yields and stereospecificity,[5] reference is made to studies in which dichloromethane and neopentane are compared as "inert" diluents.[6,13] Yet in the one communication (ref 6) there are no common concentrations of dichloromethane and neopentane and the experiments which can be roughly compared are at concentrations of 10% hydrocarbon (cyclohexene) or less at which the collisional deactivation effect of dichloromethane probably predominates over any stabilizing effect and at which the C–H insertion yields with cyclohexene are difficult to compare because of the appreciable yields of neopentylurethan which form at these high dilutions. In an accompanying communication (ref 13) data is presented on the stereospecificity of the addition of carbethoxynitrene to *cis*- and *trans*-4-methyl-2-pentene which shows that at 1.5 mol % hydrocarbon and correcting for the neopentylurethan formed, the stereospecificity of the addition reaction is the same with dichloromethane and neopentane as diluents.[13] However, in a later paper, again reporting the results of reactions of carbethoxynitrene with the 4-methyl-2-pentenes and comparing neopentane and dichloromethane as diluents, Lwowski concluded that, if anything, dichloromethane seems to stabilize the singlet relative to neopentane.[1]

Experimental Section

Reagents. Ethyl azidoformate, bp 40–41° (30 mm), was prepared from potassium azide and ethyl chloroformate.[14]

trans-1,2-Dimethylcyclohexane (Baker grade) was found to be >99% pure by vpc and was used without further purification.

Dichloromethane (Eastman reagent grade) was used without further purification.

General Reaction Procedure. Into a thick-wall tube was place approximately 2 g of *trans*-1,2-dimethylcyclohexane and approximately 0.2 g of ethyl azidoformate. The proper amount of dichloromethane was then added to give the desired mole fraction concentration of hydrocarbon. The tube was then degassed three times, sealed under vacuum, and heated for 90 hr at 120° in an oil bath. When the reaction was done at high dilution (50% hydrocarbon or less), the product mixture was concentrated by removing solvent to a volume of about 3 ml.

The products were analyzed by vpc (Aerograph A-700 gas chromatograph) with an XF-1150 column (8 ft × 0.25 in., 15% on 60/80 Chromosorb W, column temperature 155°, 60 ml/min He) and peak areas were determined by the "cut and weigh" technique. Nmr analysis of material collected from the gc was used to identify the C–H insertion products. For *trans*-1,2-dimethylcyclohexane, there is one product expected from insertion into the tertiary C–H bonds, four isomeric products from the secondary C–H bonds, and one from the primary. After the shorter retention time peaks due to solvent, unreacted hydrocarbon, and urethan are obtained, there is a large peak for the tertiary C–H insertion product (with good separation of *cis*- and *trans*-1,2-dimethylcyclohexyl-1-urethane on this column having been previously established) followed by a series of four smaller overlapping peaks (secondary insertion products) and one peak with the longest retention time (primary C–H insertion product). This order of elution (tertiary, secondary, primary) is the same as that observed by Lwowski for the isomeric 3-methylhexane urethanes.[9]

Chemical shifts, peak multiplicities, and integrated areas are consistent with the structures assigned to the insertion products collected from the gc: tertiary insertion product δ_TMS (CCl₄) 4.11

(q, J = 7.5 Hz, 2, CH$_2$ of Et), 1.28 (t, J = 7.5 Hz, 3, CH$_3$ of Et), 0.97 (d, J = 7.0 Hz, 3, CH$_3$ on tertiary C with H), 1.23 (s, 3, CH$_3$ on tertiary C with -NHCO$_2$Et), 0.9-2.3 (m, 18, all H except NH, CH$_2$ of Et); secondary insertion product δ_{TMS} (CCl$_4$) 3.93 (q, J = 7.5 Hz, 2, CH$_2$ of Et), 1.11 (t, J = 7.5 Hz, CH$_3$ of Et), 0.87 (s, 6, CH$_3$'s on tertiary C's), 1.95 (s, 1, H on C with -NHCO$_2$Et). The two methyl groups on each of the four secondary insertion products should each appear as a doublet. The singlet listed at δ 0.87 is the envelope of these closely spaced, unresolved doublets. The primary insertion product was not present in sufficient quantity for analysis and assignment was based on retention time and selectivity data.

The stereospecificty and selectivity were then calculated from the peak areas in the usual manner. The absolute yield was determined by using acetophenone as an external standard. Total moles of insertion product was then calculated from the area/mol for acetophenone using the calibration factor of 0.78 for the products relative to acetophenone. It was assumed that all the insertion products have the same detector sensitivity.

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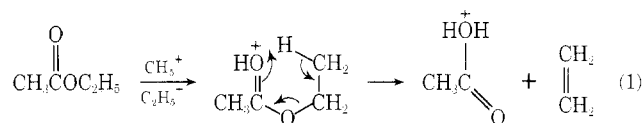(14) W. Lwowski and T. W. Mattingly, Jr., *J. Amer. Chem. Soc.*, **87**, 1947 (1965).

Studies in Chemical Ionization Mass Spectrometry. Mechanisms in Ester Spectra

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We wish to report deuterium labeling experiments on the methane chemical ionization (CI) mass spectrum of ethyl acetate which were designed to establish some of the mechanisms previously postulated to explain the observed products.[1] In the partial CH$_4$ CI mass spectrum of ethyl acetate (Table I) the major decomposition product is the protonated acid. It was suggested that this ion could be formed in the following manner.[2]

$$CH_3COC_2H_5 \xrightarrow[C_2H_5]{CH_5^+} CH_3C \cdots CH_2 \longrightarrow CH_3C + CH_2 \quad (1)$$

Table I
CH$_4$CI Mass Spectra of Ethyl Acetates

m/e	$-$CH$_2$CH$_3{}^a$	$-$CD$_2$CH$_3{}^b$	$-$CD$_2$CD$_3{}^c$
		100 I_i/Σ_i	
61	44.8	45.0	2.3
62	1.1	4.6	30.4
63	0.7	1.0	1.2
87	0.4		
88	0.6		
89	44.8	3.3	0.3
90	2.3	1.0	2.4
91		38.8	0.1
92		1.8	0.4
93			2.6
94			49.4
95			3.2

^{a} Registry no., 141-78-6. ^{b} Registry no., 51472-78-7. ^{c} Registry no., 51472-79-8.

An average CH$_4$ CI mass spectrum of CH$_3$COOCD$_2$CH$_3$ is also given in Table I. The major processes are the same for the deuterated and undeuterated species. It is apparent from Table I that reaction 1 is the dominant process, since very little deuterium is incorporated in the protonated acid ions.

From these and other data collected at different concentrations of ethyl acetate, repeller voltages of 0-2 V, source temperatures of 110-160°, and CH$_4$ pressures of 0.5-0.9 Torr, the average ratio of ionic abundances at m/e 62 and 61 was 0.109 ± 0.006. With the appropriate correction of ^{13}C, the ratio of abundances of species (CH$_3$CO$_2$HD$^+$)/(CH$_3$CO$_2$H$_2^+$) is 0.086 ± 0.006. The specificity of the decomposition process is high, but not 100%: incorporation of the deuterium atom from the α carbon occurs about 8% of the time, and reaction 1 occurs about 92% of the time.

It is of interest to compare the rearrangement decomposition of protonated ethyl acetate in the CH$_4$ CI mass spectrum with the rearrangement decomposition of the molecular ion of ethyl acetate in the electron ionization (EI) mass spectrum. The formation of CH$_3$COOH$^+$ from the molecular ion by the McLafferty rearrangement is the comparable process, involving the transfer of only one H (or D) atom. The observed ratio[3] for (CH$_3$COOH$^+$)/(CH$_3$COOD$^+$) from the high-voltage EI spectrum of CH$_3$COOCD$_2$CH$_3$ was 0.7:0.3.

Appreciable scrambling occurs prior to decomposition of the radical molecular ions, M·$^+$, produced by electron ionization. Little scrambling occurs prior to the decomposition of the even-electron (M + H)$^+$ ions produced in the methane CI spectra.

In the CH$_4$ CI spectra of alkyl esters, there were observed[1] ions of the type RCOHOC$_2$H$_5^+$. It was suggested that these "alkyl exchange" ions could be the result of the decomposition of an intermediate ethyl addition (M + C$_2$H$_5$)$^+$ ion (which is observed under some conditions in the CH$_4$ CI spectra of esters). This (M + C$_2$H$_5$)$^+$ ion can decompose in two ways (eq 2a and 2b).

Reactions 2a and 2b are, of course, indistinguishble for the unlabeled esters (R' = H), but would give different products if the original alkyl group were propyl or higher (R' = CH$_3$, ...). Differentiable products will be produced if the original alkyl group of the ester is labeled, CH$_3$COOCD$_2$CH$_3$ and CH$_3$COOCD$_2$CD$_3$.

If the proposed mechanism is correct, the displacement reaction (2a) should give CH$_3$CO$_2$HC$_2$H$_5^+$ ions at m/e 89 in the spectrum of CH$_3$CO$_2$CD$_2$CH$_3$ and CH$_3$CO$_2$DC$_2$H$_5^+$ ions at m/e 90 in the spectrum of CH$_3$CO$_2$CD$_2$CD$_3$. Reaction 2b will give (M + H)$^-$ ions at m/e 91 and 94 for these two esters. Reaction 2b cannot be resolved from proton transfer from CH$_5^+$.