g (22% based on unrecovered starting material) of the aldehyde (**8**), bp 85° (6 mm), and 0.66 g of starting material. The aldehyde was immediately dissolved in 4 ml of trimethyl orthoformate, 0.20 g of *p*-toluenesulfonic acid monohydrate was added, and the reaction was stirred for 12 hr at room temperature. The temperature was then held at 65–75° for 12 hr while allowing methyl formate to distill off through a short-path distillation apparatus. After cooling, the reaction mixture was extracted twice with 2-ml portions of cold 4 *N* hydrochloric acid. The acid extracts were immediately made basic with saturated potassium bicarbonate solution and extracted ten times with 10-ml portions of ether. The ethereal extracts were dried over anhydrous magnesium sulfate, the desiccant was removed, and the filtrate was concentrated by distillation of the solvent. The residue was shown to have the same vpc retention time as the degradation product from **2** using a 10 ft × $^1/_8$ in. column of SE-30 on Fluoropak at 160°, and also a 10 ft × $^3/_8$ in. column of 20% (4:1) Apiezon L–KOH on 60–80 firebrick at 138°. Preparative vapor phase chromatography using the latter column afforded a pure sample of 1-methyl-4-(2,2-dimethoxyethyl)-piperidine having an infrared spectrum identical with that of the product from degradation of **2**.

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Nonpolar Solvent Effects. II. Nuclear Magnetic Resonance Evidence for Complex Formation

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We have recently reported[1] significant solvent effects upon the Curtius reaction of 2-naphthoyl azide and *o*-nitrobenzoyl azide in nonpolar solvents. No satisfactory correlation of the reaction rates with bulk solvent properties was found. Consequently, the nature of the solutions of 2-naphthoyl azide in several nonpolar solvents has been investigated by means of nuclear magnetic resonance spectroscopy (nmr), and the results are reported herein.

One spectrum is shown in Figure 1. Data for the spectra are given in Table I. Complete analysis of the 2-naphthoyl azide spectrum is not necessary for the purposes of this study. Partial analysis of nmr spectra of substituted naphthalenes has been made[2] as well as a complete analysis of the spectrum of naphthalene[3] itself. The low-field resonance (A in Figure 1) may be assigned to the α hydrogen *ortho* to the carbonyl group based on the following: α hydrogens appear at lower field than β hydrogens;[2,3] aromatic hydrogens are deshielded by *ortho* carbonyl groups;[4] the low-field resonance in the spectrum of 2-acetonaphthone has been assigned to the α hydrogen *ortho* to the carbonyl group;[2] and finally, the integration curve for the spectrum of 2-naphthoyl azide shows that the low-field resonance is equivalent to one hydrogen.

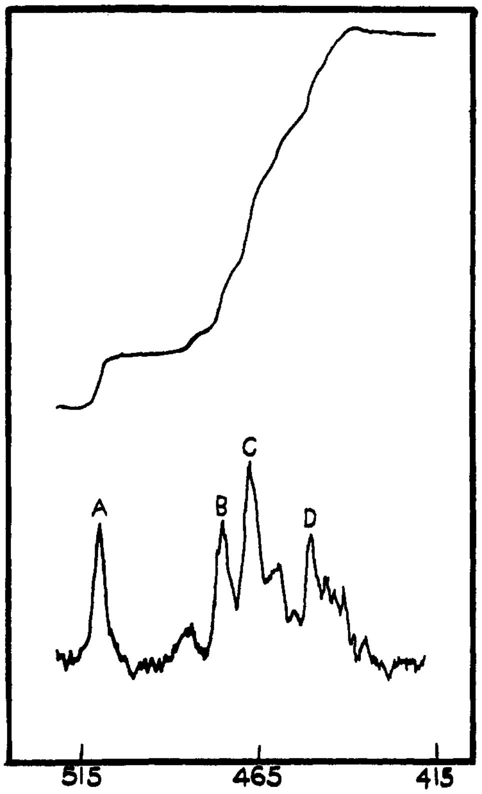

Figure 1.—Nmr spectrum of 2-naphthoyl azide in cyclohexane solution at 47.5°. Details are in the text.

The chemical shifts of the protons of a solute molecule are affected by the following factors when the solvent is changed:[5–8] hydrogen bonding, van der Waals interactions, bulk magnetic susceptibilities of the solvents, solvent magnetic anisotropies, reaction field effects, specific solute–solvent interactions, and changes in conformational populations.[9] Use of an internal reference eliminates solvent anisotropy effects if no specific solute–solvent interactions are present[7] and also solvent bulk magnetic susceptibility effects in any case.[6] Hydrogen bonding does not occur in the present system. The use of the dilute solutions in this study eliminates solute–solute interactions except for specific solute–solute complexing. Shifts owing to van der Waals interactions should be diminished by use of an internal reference and similar type solvents.[6] The high-temperature spectra obtained in the four hydrocarbon solvents are all the same within experimental error; therefore, at that temperature in these solvents none of the effects contributing to solvent shifts listed above have any significance, *i.e.*, these solutions are purely physical solutions in this temperature range. Table II shows the effect of temperature on the spectra in each solvent. The change in the spectral positions with temperature variation is within experimental error with all solvents except *n*-heptane (and possibly 1-octene). This temperature effect in the *n*-heptane solutions could be

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[1] D. C. Berndt, M. Zuika, and M. S. Clark, Jr., *Chem. Ind.* (London), 139 (1965).

[2] G. O. Dudek, *Spectrochim. Acta*, **19**, 691 (1963).

[3] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 147 ff, 247 ff.

[4] J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall Co., Inc., Englewood Cliffs, N. J., 1965, p 79.

[5] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

[6] J. V. Hatton and W. G. Schneider, *Can. J. Chem.*, **40**, 1285 (1962).

[7] W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).

[8] A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

[9] G. M. Whitesides, J. J. Grocki, D. Holtz, H. Steinberg, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1058 (1965).

TABLE I

CHEMICAL SHIFTS[a] OF 2-NAPHTHOYL AZIDE IN SEVERAL SOLVENTS AT VARIOUS TEMPERATURES[b]

	Position[c]											
Solvent	A	B	C	D	A	B	C	D	A	B	C	D
		3.5°				25.5°				47.5°		
Carbon tetrachloride	513	477.5	474	457.5	512	477	473	457	512	476	472	455.5
		12°				29°				47.5°		
Cyclohexane	510.5	476	468	452	511	475.5	467.5	451	509.5	475	467.5	450.5
		12°				31°				49°		
Cycloheptane	511	476	468.5	452	510	475.5	468	451.5	509.5	475	468	451
		10°				29°				46°		
1-Octene	513	479.5	470.5	454	512	478	469	452.5	511	476	468.5	452
		10°				29°				47.5°		
n-Heptane	513	478.5	470	453	511	477	468	452	510	475.5	467	450.5
Max Δ per column, all solvents	2.5	3.5	6.0	5.5	2.0	2.5	5.5	6.0	2.5	1.0	5.0	5.0
Max Δ all solvents except CCl_4	2.5	3.5	2.5	2.0	2.0	2.5	1.5	1.5	1.5	1.0	1.5	1.5

[a] Cycles per second downfield from TMS to nearest 0.5 cps. [b] Temperature appears immediately above cycles per second data to which it refers. [c] See Figure 1.

due to changes in conformational populations and/or to weak complexing[6,10] at the lower temperatures. Conformational effects resulting from hindered rotation about the carbonyl carbon–phenyl carbon bond of benzaldehyde have been observed at very low temperatures.[11] Similar conformational effects are considered unlikely with 2-naphthoyl azide in the present system in which the temperatures are much higher than those employed in the benzaldehyde study. Solute–solvent complex formation seems unlikely with an alkane solvent; consequently, it is suggested that solute–solute association occurs in *n*-heptane at the lower temperatures. Considerable evidence for this type of molecular association exists[12] and the term "multipolar complex" has been suggested[12] for this association—the bonding is the result of dipole–dipole attraction between the polar groups of the molecules. The dimerization of nitrobenzene in carbon tetrachloride solution serves as an example.[12] The chemical shift associated with multipolar complexing is generally toward lower field for both molecules involved in the complex.[12] Our present results for 2-naphthoyl azide in *n*-heptane (and possibly 1-octene) solution are consistent with the above picture.

TABLE II

DIFFERENCE IN CHEMICAL SHIFT BETWEEN EXTREME TEMPERATURES

	Δ, cps[a] at position			
Solvent	A	B	C	D
Carbon tetrachloride	1	1.5	2	2
Cyclohexane	1	1	0.5	1.5
Cycloheptane	1.5	1.0	0.5	1.0
1-Octene	2	3.5	2	2
n-Heptane	3	3	3	2.5

[a] Shift (downfield from TMS) at lowest temperature minus shift at highest temperature.

The resonance positions C and D for 2-naphthoyl azide in carbon tetrachloride solution are shifted (5–6 cps) with respect to positions A and B compared with corresponding resonance positions in the other solvents; *i.e.*, an internal shift[13] occurs. Internal shifts with a change in solvent result from three factors: changes in conformational populations,[9] reaction field effects,[5,8] and specific solute–solvent complexing.[13] Conformational effects involving the azido carbonyl group are considered unimportant as a cause of the internal shifts in the present system—the position of the singlet (peak A, Figure 1) owing to the α proton *ortho* to the carbonyl group undergoes a change from within to slightly without experimental error as the solvent is varied while the internal shifts for peaks C and D are rather large. Reaction field effects are more inportant with solvents of high dielectric constant[13] and can be eliminated as a cause of internal shifts in the present system by comparison of the results in *n*-heptane and cyclohexane solvents at 29°. There is no significant difference in the spectra in these two solvents which differ almost as much in dielectric constant (at 20°) as do carbon tetrachloride and cyclohexane. The internal shifts which occur when carbon tetrachloride is substituted for the hydrocarbon solvents (in which no complexing occurs at about 50°) are therefore attributed to complex formation between carbon tetrachloride and 2-naphthoyl azide. Formation of complexes of carbon tetrachloride with benzene, *p*-xylene, mesitylene, and hexamethylbenzene has been reported.[14,15]

Benzene, carbon tetrachloride, 1-octene, cyclohexane, and *n*-heptane were the solvents used in the rate studies[1] of the Curtius reaction of 2-naphthoyl azide at 65.6°. In view of the above nmr results, true physical solutions exist only in the solvents 1-octene, cyclohexane, and *n*-heptane at 65.6°. Since the chemical shifts in carbon tetrachloride showed little, if any, change over the temperature range 3.5 to 47.5°, it seems likely that the complex between carbon tetrachloride and 2-naphthoyl azide would exist at 65°. Nmr measurements with benzene as solvent are not possible because of absorption owing to the solvent, nevertheless, it seems likely that some type of specific solute–solvent interaction would exist in the benzene solutions in view of the several reports of benzene–solute interac-

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(10) R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **40**, 2329 (1962).

(11) F. A. L. Anet and M. Ahmed, *J. Am. Chem. Soc.*, **86**, 119 (1964).

(12) See R. W. Taft, G. B. Klingensmith, and S. Ehrenson, *ibid.*, **87**, 3620 (1965), and references cited therein.

(13) T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, **32**, 1218 (1960).

(14) J. R. Goates, R. J. Sullivan, and J. B. Ott, *J. Phys. Chem.*, **63**, 589 (1959).

(15) F. Dorr and G. Buttgereit, *Ber. Bunsenges. Physik. Chem.*, **67**, 867 (1963).

tions.[7,10,13,14,16] Unless the effects of the specific solute–solvent interactions in carbon tetrachloride and benzene solutions are minor compared with the effects produced by variation in bulk solvent parameters, the use of these parameters is limited to 1-octene, cyclohexane, and *n*-heptane in the present system. Of the parameters listed before,[1] only the dielectric constant function, $(D - 1)/(2D + 1)$, computed from values[17] at 20°, gives a good linear relation with log k for these three solvents. The point for carbon tetrachloride lies somewhat off and for benzene considerably off the line for the above three solvents. Use of the above dielectric constant function may not be valid, however, for solvents of low dielectric constant.[18]

In view of the results reported here, it is clear that conclusions regarding reaction mechanisms based on nonpolar solvent effects should be based on studies in solvents of widely varying character.

Experimental Section

The 2-naphthoyl azide was prepared and solvents were purified as before[1] (cycloheptane purified as was cyclohexane). Solvents were deoxygenated before use by passing dry nitrogen through them. The spectra were determined with solutions 0.10 *M* in 2-naphthoyl azide with 0.1% by volume of tetramethylsilane (TMS) as internal standard at a 500-cps sweep width (TMS at +15 cps) with a Varian A-60 spectrometer. The reproducibility of the chemical shifts relative to internal TMS is within 0.5 cps in most instances, 1 cps being the largest variance. Temperatures at which the spectra were determined were ascertained by comparison of the differences in the resonance positions of methanol or ethylene glycol with the corresponding values in the Varian charts.

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(16) J. Tyrrell, *Can. J. Chem.*, **43**, 783 (1965).

(17) See ref 1. Dielectric constant for 1-octene: A. P. Altshuller, *J. Phys. Chem.*, **59**, 32 (1955). Density of 1-octene at 65.6° is 0.675 g/ml.

(18) R. G. Pearson [*J. Chem. Phys.*, **20**, 1478 (1952)] states that $x = \mu^2/r^3DkT$ should be less than one for the function $(D - 1)/(2D + 1)$ to be valid. For $T = 338°$K and $D = 2$ with μ and r arbitrarily chosen as 2 D. and 3 A, respectively, $x = 1.6$.

The Preparation of Ethyl Diazoacetate *via* a Triazene Intermediate

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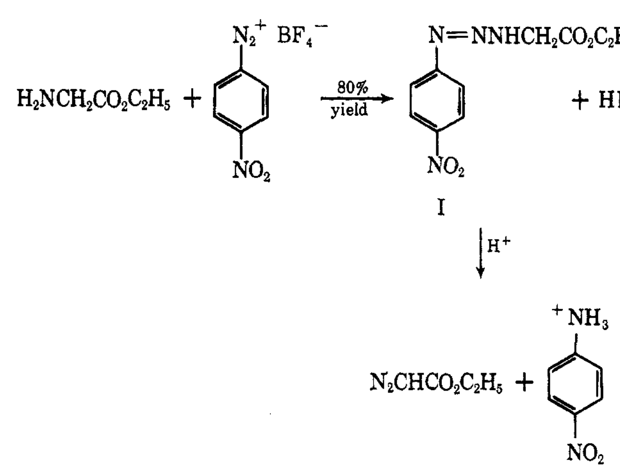
Ethyl diazoacetate has been prepared *via* the acidic decomposition of N-(*p*-nitrophenylazo)glycine ethyl ester (I). The triazene derivative I is readily formed from the ethyl ester of glycine and *p*-nitrobenzenediazonium fluoroborate (eq 1).

Evidence in support of the triazene structure is provided by the method of preparation, the elemental analysis, the infrared spectrum (see the Experimental Section), and by the reaction of thet riazene (I) with acid to give ethyl diazoacetate and *p*-nitroaniline.[1a] The ethyl diazoacetate obtained from triazene I gave an infrared spectrum which was identical with the infrared spectrum of the ethyl diazoacetate prepared by the nitrous acid procedure[1] and by the nitrosoamide pyrolysis reaction.[2] Likewise the 3,5-dinitrobenzoate ester derivative obtained by the reaction of the triazene derived ethyl diazoacetate with 3,5-dinitrobenzoic acid, was identical with the 3,5-dinitrobenzoate ester derivative obtained from the ethyl diazoacetate prepared by the other two procedures.[2]



(1)

The major advantage of the triazene method for obtaining ethyl diazoacetate over the nitrous acid procedure is that strong acids are not required at any stage. Strong acids also are not used in the nitrosoamide pyrolysis procedure, but the nitrosoamide sequence involves three steps.[2]

The production of ethyl diazoacetate from triazene I is also of interest in connection with the mechanism of the triazene deamination. The triazene deamination reaction probably proceeds through intermediates which are analogous to the intermediates established for the mechanism of the nitrosoamide deamination reaction (eq 2 and 3).[2–6] Thus, it has been established by White and co-workers, Huisgen and co-workers, and others that nitrosoamides of primary carbinamines form intermediate diazoalkanes during the pyrolytic deamination (eq 3a).[2,3,6] The isolation of ethyl diazoacetate from the pyrolysis of ethyl N-carbethoxy-N-nitrosoglycinate[2] is one of the pieces of evidence which supports the diazoalkane pathway. The diazoalkane route (3a) presumably is followed during the pyrolysis of those nitrosoamides which give rise to unfavorable carbonium ions (*e.g.*, primary carbonium

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[1a] NOTE ADDED IN PROOF.—Additional evidence has been obtained for the triazene structure I. The mass spectrum of I (mol wt 252; a principal peak at 150, corresponding to the *p*-nitrophenyldiazonium ion) and the nmr spectrum of I were consistent with the assigned structure. The mass spectrum and nmr spectrum were run at the Noyes Laboratory, The University of Illinois, Urbana, Ill.

(1) N. E. Searle, *Org. Syn.*, **36**, 25 (1956).

(2) E. H. White and R. J. Baumgarten, *J. Org. Chem.*, **29**, 2070 (1964).

(3) E. H. White and C. A. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, **83**, 1174, 1179 (1961), and references therein.

(4) E. H. White and H. Scherrer, *Tetrahedron Letters*, 758 (1961).

(5) M. Schroeder and E. H. White, the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract S-54.

(6) R. J. Baumgarten, *J. Chem. Educ.*, **43**, 398 (1966).