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.

Acknowledgment.—The author wishes to thank Dr. D. C. Iffland and Mr. J. L. Schoolenberg for operation of the nmr spectrometer, the National Science Foundation for a grant to the university making the purchase of the spectrometer possible, and the donors of the Department of Chemistry Summer Faculty Fellowship Program for financial support.

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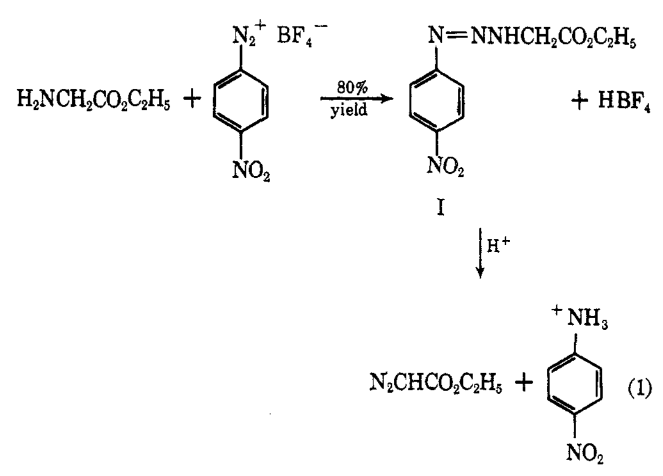
Ethyl diazoacetate has been prepared *via* the acidic decomposition of N-(*p*-nitrophenylazo)glycine ethyl ester (I). The triazene derivative I is readily formed from the ethyl ester of glycine and *p*-nitrobenzenediazonium fluoroborate (eq 1).



I

(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]

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).

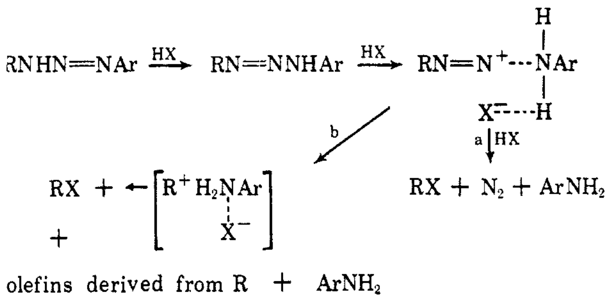
[3] E. H. White and C. A. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, **83**, 1174, 1179 (1961), and references therein.

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

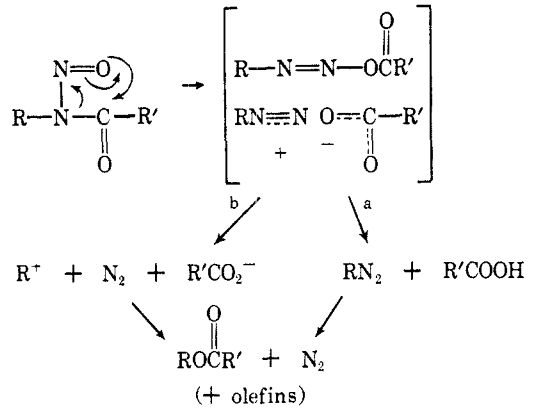
[5] M. Schroeder and E. H. White, the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract S-54.

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

ions).[7] Only those diazoalkanes which possess special stabilizing structural features such as the conjugated α-carbonyl functionality in ethyl diazoacetate are, however, isolable under the reaction conditions.[2] These same considerations apparently apply similarly to the acidic deaminations of the triazenes (eq 2),[4,5]



(2)



(3)

and the present isolation of ethyl diazoacetate by the acidic hydrolysis of triazene I provides further support for the analogy.

The yields of ethyl diazoacetate from triazene I are *ca.* 30–66%. Purified triazene I reacts rapidly with hydrochloric acid and slowly with 3,5-dinitrobenzoic acid at 25° to give the ethyl diazoacetate. Purified triazene I does not give ethyl diazoacetate with water or basic solutions at 25°. Likewise attempts to pyrolyze neat purified triazene I or purified triazene I in the presence of base (*e.g.*, *p*-nitroaniline) gave, at best, trace amounts of ethyl diazoacetate. On the other hand, pyrolysis of the crude triazene I product (obtained as shown in eq 1) gives ethyl diazoacetate in good yield. This pyrolysis may either occur as a result of the presence of acidic impurities in the crude triazene I preparation, or this pyrolysis may proceed by some other mechanism, such as a free-radical one, under these conditions.

Experimental Section

The *p*-nitrobenzenediazonium fluoroborate was purchased from Eastman and the glycine ethyl ester hydrochloride was Eastman reagent grade. Infrared spectra were obtained on the Beckman IR-10.

N-(*p*-Nitrophenylazo)glycine Ethyl Ester (I).—Sodium carbonate (2.76 g, 26.0 mmoles) was dissolved in 55 ml of distilled water. Methylene chloride (150 ml) was added. Glycine ethyl ester hydrochloride (6.98 g, 50.0 mmoles) was then added to the above ice–salt cooled mixture at 0° over a period of 15 min while the solution was being stirred. After another 10 min of stirring, *p*-nitrobenzenediazonium fluoroborate (10.4 g, 43.9 mmoles, mp 156° dec) was added to the mixture over a period of 30 min at 0°, while the solution was being stirred. The reaction mixture was slowly allowed to warm to 28°. After 4 hr more, the reaction mixture was filtered. The insoluble material was largely unreacted fluoroborate. The methylene chloride layer was separated from the water layer, after which the methylene chloride portion was washed with water and dried over sodium sulfate. *In vacuo* removal of the methylene chloride, gave 8.10 g (32.0 mmoles, 72.9%) of crude yellow triazene I, mp 92–94°. Recrystallization of I from hexane gave yellow needles melting at 96–98°.

Anal. Calcd for $C_{10}H_{12}N_4O_4$: C, 47.62; H, 4.80; N, 22.22. Found: C, 47.68; H, 4.86; N, 22.22; mol wt, 252 (mass spectrum).

The infrared spectrum (methylene chloride) showed 3440 (wbr), 3320 (w), 1750 (ms), 1610 (m), 1520 (ms), 1395 (wbr), 1380 (w), 1340 (vs), 1220 (sh), 1190 (ms), 1165 (m), 1115 (m), 1025 (w), 980 (w), 860 (sh), and 850 (m) cm^{-1} principal peaks.

The triazene apparently is a stable compound which may be stored indefinitely.

Ethyl Diazoacetate.—Sodium carbonate (5.0 g, 47.8 mmoles) was dissolved in 100 ml of distilled water. Methylene chloride (150 ml) was added and the reaction mixture was cooled to 0–5°. Glycine ethyl ester hydrochloride (6.85 g, 49.0 mmoles) was then added over a period of 15 min to the reaction mixture, while the mixture was being stirred at 5°. After 10 min more, *p*-nitrobenzenediazonium fluoroborate (11.0 g, 46.4 mmoles, mp 146° dec) was added to the mixture over a period of 30 min at 5°, while the mixture was being stirred. The reaction mixture slowly was allowed to warm to 28°, after which 100 ml more of methylene chloride was added. The mixture was then stirred for 20 hr more, after which time it was suction filtered. The methylene chloride layer was then separated and dried over sodium carbonate. *In vacuo* evaporation of the methylene chloride gave 9.92 g (39.4 mmoles, 84.7%) of crude triazene I, mp 80–95° (authentic I had mp 96–98°). The crude triazene was dissolved in 100 ml of methylene chloride and stirred for 20 hr with 100 ml of 6% acetic acid saturated with sodium chloride. The methylene chloride layer was then separated and washed with a saturated sodium carbonate solution. After the methylene chloride layer was separated, it was dried over potassium carbonate and filtered. The methylene chloride was then removed *in vacuo* and the remaining product was vacuum distilled (20–50 mm) over a boiling-water bath to give 3.20 g (30.8 mmoles, 66.4%) of yellow ethyl diazoacetate. The infrared spectrum of this ethyl diazoacetate (3,5-dinitrobenzoate derivative mp 59–60°, lit.[2] mp 59–60°) was identical with the infrared spectrum of ethyl diazoacetate prepared by the nitrous acid procedure.[1] If the crude product was distilled under higher vacuum (<1 mm), the ethyl diazoacetate was contaminated with *p*-nitroaniline.

Ethyl diazoacetate also was obtained in 35% yield upon pyrolysis of crude triazene I without the prior acetic acid treatment. In fact, even after the acetic acid hydrolysis step, only a small amount of ethyl diazoacetate was evident in the product with the bulk of the material being triazene I as determined from the infrared spectrum. Most of the ethyl diazoacetate is apparently produced upon the heating of the crude product mixture.

Ethyl diazoacetate is also produced in varying yields upon treatment of the purified triazene I with 3 *N* hydrochloric acid and upon pyrolysis of the purified triazene I with such acids as 3,5-dinitrobenzoic acid and glycine ethyl ester hydrochloride.

Ethyl diazoacetate may also be obtained in *ca.* 35% yield *via* the treatment of the triazene I with a 2:1 excess of 3,5-dinitrobenzoic acid in methylene chloride at 28° for 3 days.

Proper safety precautions should be taken in all pyrolyses involving ethyl diazoacetate even though no explosions were presently encountered.

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(7) Nitrosoamides of secondary and tertiary carbinamines, on the other hand, have been shown to produce ion-pair intermediates (eq 3b) on pyrolysis.