washed with 5% Na_2CO_3 and water and dried ($MgSO_4$) and the ether was removed under reduced pressure. The faintly yellow liquid which remained was ethyl allylnitrosocarbamate (17.1 g, 91%); nmr (neat): τ 8.66 (3 H, methyl, t, J = 7 Hz), 5.47 (2 H, ester methylene, q, J = 7 Hz), 5.63 (2 H, N-methylene), and 4.00–5.17 (3 H, vinyl protons, m).

A solution of 10 mmol of the ethyl allylnitrosocarbamate in 20 ml of cyclohexene was added (5 min) to a mixture of 30 ml of cyclohexene and 10 ml of 3 *N* methanolic sodium methoxide solution (30 mmol). The mixture was stirred in the dark under nitrogen at +4° (ice bath) for 90 min, then extracted with cold 10% aqueous sodium hydroxide (two 50-ml portions) and the clear, red solution of diazo compound in cyclohexene was dried over potassium hydroxide pellets for 10 min at 4°. The yield, determined by the amount of N_2 evolved on treatment with acid, was 65%. The solution had a λ_{max} at 486 mμ (ϵ 19.4). A quantitative yield of pyrazole (mp ir, nmr) was obtained when a solution of 3-diazopropene in cyclohexane was allowed to stand in the dark at room temperature for 48 hr.

Rate of Pyrazole Formation from 1,3-Bisdiazopropane. Hexamethylbenzene (0.1228 g) was dissolved in 40 ml of a cyclohexene solution of 1,3-bisdiazopropane which had been prepared from 1.18 g of crude potassium propane-1,3-bisdiazotate. The solution was poured into a black bottle which was placed in a constant-temperature bath at 25.0°. At various time intervals a 1.00-ml aliquot of the yellow solution was removed and added to a vial containing one drop of acetic acid. The acid destroyed any diazo compound present. The samples were analyzed for pyrazole by glpc using hexamethylbenzene as an internal standard. A 5-ft column packed with 10% Carbowax 20M on Fluoropak 80 was used at 215° with a helium flow rate of 20 cc/min. At the time the first sample was withdrawn there was 2.69 mmol of 1,3-bisdiazopropane in the solution (40.5 ml). This figure was obtained by measuring the absorbance of the solution at 462 mμ (ϵ 27.4). The rate constant for pyrazole formation at 25° was $9.8 \pm 0.4 \times 10^{-5}$ sec^{-1}.

Rate of Pyrazole Formation from 3-Diazopropene. The rate of disappearance of diazoalkene was followed through the decrease of absorbance at 486 mμ. A cyclohexene solution of the diazoalkene in a black bottle was placed in a constant-temperature bath at 25.0°. Samples were removed periodically and the absorbance was measured quickly. Plots of $\log (A - A_\infty)$ *vs.* time were linear. Three measurements gave $k_1 = 6.03 \pm 0.03 \times 10^{-5}$ sec^{-1}.

Acknowledgment. We are indebted to the Graduate Council of Michigan State University and to the National Science Foundation for financial support of this work.

The Cyclization of 3-Diazoalkenes to Pyrazoles

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Received September 9, 1968

Abstract: Eight 3-diazoalkenes have been prepared from the related ethyl alkenylnitrosocarbamates and methanolic sodium methoxide. All of these unsaturated diazo compounds spontaneously cyclized at room temperature to form pyrazoles in essentially quantitative yields. The cyclizations were cleanly unimolecular. The first-order rate constants for the reactions of four substituted *trans*-3-diazo-1-phenylpropenes fit the Hammett equation (ρ = −0.40). The relative insensitivity of the cyclization rates to the electronic nature of substituents suggests that the reaction is an intramolecular 1,3-dipolar cycloaddition.

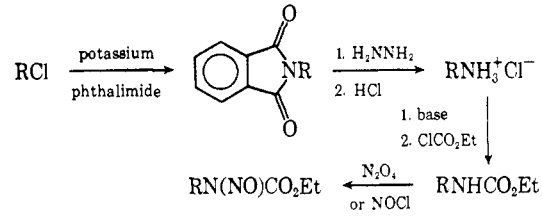
In 1935 it was briefly reported that 3-diazopropene slowly decomposed at room temperature to give pyrazole.[2,3] Adamson and Kenner[2] also noted that the decomposition was unimolecular and accelerated by light. Recently, Ledwith and Parry reported the results of a more detailed investigation of the relatively modest effect of light on the rate at which 3-diazopropene cyclizes.[4] Adamson and Kenner also observed that the red color of an ethereal solution of *trans*-1-diazo-2-butene slowly faded at room temperature. The product of this decomposition was not identified; later, Curtin and Gerber[5] showed that it was 3(5)-methylpyrazole.

The present report describes the cyclization of these and six additional 3-diazoalkenes. The rates at which these compounds thermally isomerize to pyrazoles were measured. The effect of substituents on these rates contributes to an understanding of the reaction mechanism.

(1) Michigan State University Graduate Council Fellow, 1965–1966; National Science Foundation Predoctoral Fellow, 1966–1967.
(2) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 286 (1935).
(3) C. D. Hurd and S. C. Lui, *J. Am. Chem. Soc.*, 57, 2656 (1935).
(4) A. Ledwith and D. Parry, *J. Chem. Soc., B*, 41 (1967).
(5) D. Y. Curtin and S. M. Gerber, *J. Am. Chem. Soc.*, 74, 4052 (1952).

Results

Ethyl alkenylnitrosocarbamates, the precursors of the 3-diazoalkenes, were prepared using the synthetic sequence shown. In the final step, either of two reagents was used to nitrosate the ethyl alkenylcarbamate. Di-



nitrogen tetroxide reacted cleanly with all the carbamates not containing an aromatic ring to give the corresponding N-nitroso analogs in nearly quantitative yield. The aryl-substituted alkenylcarbamates, however, were only partially converted to the corresponding alkenylnitrosocarbamates by an equimolar amount of dinitrogen tetroxide even though all of the dinitrogen tetroxide was consumed. Evidently a portion of the reagent was lost in side reactions, possibly electrophilic

attack on the aromatic ring or the double bond. Three ethyl *trans*-3-aryl-2-propenylnitrosocarbamates were prepared in nearly quantitative yield using the milder nitrosating agent,[6] nitrosyl chloride in pyridine solution. This reagent was usually used at −5°, but with *trans*-3-(*p*-tolyl)-2-propenylcarbamate it was necessary to reduce the temperature to −20°; even so, this nitrosocarbamate was isolated in only 43% yield.

The yellow nitrosocarbamates showed no sign of deterioration when stored in a refrigerator for 3 months. The solid compounds were purified by recrystallization; however, the crude liquid nitrosocarbamates were used without further purification. The absence of an N–H stretching band in the infrared spectra of these products indicated that they were free of any unreacted starting materials.

Solutions of the 3-diazoalkenes were prepared by stirring cyclohexene solutions of the ethyl alkenylnitrosocarbamates with methanolic sodium methoxide at 4° for 0.5–2.5 hr. The reaction mixtures were quickly washed with cold, dilute sodium hydroxide and the clear

$$RN(NO)CO_2Et \xrightarrow[CH_3OH]{NaOCH_3} (RH)N_2 + \text{ethers} + CH_3O\overset{\overset{O}{\|}}{C}OEt$$

red solutions of 3-diazoalkenes were dried briefly over potassium hydroxide pellets at 4°. The yields of 3-diazoalkenes were determined by measuring the volume of gas evolved when samples of the solutions were added to a solution of *p*-nitrobenzoic acid in diglyme. Table I lists these yields, as well as the most prominent long-wavelength absorption of the solutions.

Table I. Yields and Visible Spectroscopic Data for 3-Diazoalkenes

Diazoalkene	Yield, %	λ, mμ (ε)
3-Diazopropene	65	486[a] (19)
3-Diazo-2-methylpropene	60	492[a] (19)
trans-1-Diazo-2-butene	26	502[a] (24)
3-Diazo-1-butene	10	512[a] (?)
trans-3-Diazo-1-(*m*-nitrophenyl)-propene	41	490[b] (56)
trans-3-Diazo-(*p*-chlorophenyl)-propene	33	500[b] (64)
trans-3-Diazo-1-phenylpropene	16	504[b] (38)
trans-3-Diazo-1-(*p*-tolyl)propene	23	...

[a] Maximum. [b] Shoulder.

Alkenyl methyl ethers were also produced simultaneously with the diazoalkenes, the relative amount of the two types of product depending on the structure of the R group.[7] These ethers did not interfere with the study of the cyclization reaction.

When the red 3-diazoalkene solutions were allowed to stand in the dark at room temperature, the color slowly faded and the corresponding pyrazole was produced. Table II lists the yields of pyrazoles produced in these reactions. The pyrazoles were isolated and identified by comparing their physical and spectroscopic properties with those reported in the literature. During the preparation of a 3-diazoalkene, a small portion of the compound cyclized to the related pyrazole. The yield of pyrazole therefore had to be obtained by measuring the amount of pyrazole and 3-diazoalkene present in the solution at a particular instant, then noting the increase in the amount of pyrazole after all the 3-diazoalkene had cyclized. Two of the diazo compounds, 3-diazo-1-butene and *trans*-3-diazo-1-(*p*-tolyl)propene, cyclized so rapidly that reliable values for the yields of the pyrazoles produced from these compounds were not obtained.

The concentrations of 3-diazoalkenes in solution were determined spectroscopically using extinction coefficients which had previously been determined from solutions whose diazoalkene content was measured by observing the volume of nitrogen evolved when these solutions were added to acid. For some of the diazo compounds that were obtained only in dilute solutions, the errors in these latter measurements were probably of the order of 10–15%. Within the limits of these errors, Table II shows that pyrazoles were produced from 3-diazoalkenes essentially quantitatively.

The rate at which the concentration of 3-diazoalkenes decreased with time at 25.0° was followed spectrophotometrically. The decompositions were cleanly unimolecular. Plots of log $(A - A_\infty)$ *vs.* time were linear in all cases. Table II lists the first-order rate constants calculated from these data. The precision is indicated by the observed rate constants for 3-diazopropene itself (6.00, 6.03, and 6.08 × 10^{-5} sec^{-1}). In other cases single measurements were made because of the small amounts of materials available. There is no reason to believe that these measurements are any less precise.

The rate constants for the four aryl 3-diazoalkenes gave an excellent fit with the Hammett equation. The ρ value for the reaction was −0.40 and the correlation constant, r,[8] was 0.998.

Discussion

The eight 3-diazoalkenes described in this article all spontaneously cyclize to pyrazoles. Apparently this is a general reaction of this class of diazo compounds. Ledwith and Parry[4] suggested that the conversion of 3-diazopropene to pyrazole should be considered as an intramolecular 1,3-dipolar cycloaddition reaction. 1,3-Dipolar cycloadditions proceed by a concerted cyclic shift of electrons in which there is little change in the charge separation in the transition state relative to the ground states of the reactants.[9] For this reason the rates of 1,3-dipolar cycloadditions are relatively insensitive to the electron-donating or electron-withdrawing power of substituents attached to the dipolarophile. For example, Huisgen[9a] reported that ρ for the reaction of C-phenyl-N-methylnitrone and *para*-substituted styrenes was only +0.83. We observed that the rate of cyclization of substituted *trans*-3-diazo-1-phenylpropenes (**1**) was only 2.3 times larger when X was *p*-methyl than when X was *m*-nitro. The ρ for this reaction was only −0.40. This lack of sensitivity of the cyclization

(6) E. H. White, *J. Amer. Chem. Soc.*, 77, 6008 (1955).

(7) The effect of the alkenyl group structure on the partition of the reaction of ethyl alkenylnitrosocarbamates and base between paths leading to diazo compound and to solvolysis products is discussed in the following paper.

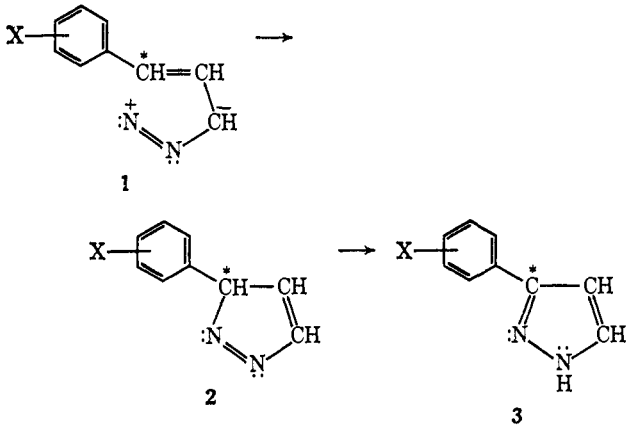
(8) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(9) (a) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, 2, 633 (1963); (b) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968); (c) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, 7, 321 (1968).

Table II. Products and First-Order Rate Constants for the Isomerization of 3-Diazoalkenes to Pyrazoles in Cyclohexene Solution at 25.0°

Diazoalkene	Product (yield, %)	$k \times 10^5$, sec^{-1}
trans-1-Diazo-2-butene	3(5)-Methylpyrazole (109)	4.51
3-Diazo-2-methylpropene	4-Methylpyrazole (100)	5.15
3-Diazopropene	Pyrazole (100)	6.03
trans-3-Diazo-1-(*m*-nitrophenyl)propene	3(5)-(*m*-Nitrophenyl)pyrazole (89)	19.3
trans-3-Diazo-1-(*p*-chlorophenyl)propene	3(5)-(*p*-Chlorophenyl)pyrazole (87)	31.2
trans-3-Diazo-1-phenylpropene	3(5)-Phenylpyrazole (86)	36.4
trans-3-Diazo-1-(*p*-tolyl)propene	3(5)-(*p*-Tolyl)pyrazole[a]	44.3
3-Diazo-1-butene	3(5)-Methylpyrazole[a]	78.5

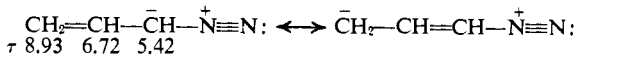
[a] Yield not determined.



X = *m*-NO_2, *p*-Cl, H, *p*-CH_3

rate to the electronic nature of X supports the belief that the reaction involves a synchronous, cyclic electron shift.

The small rate-enhancing effect of electron-donating groups may be rationalized as follows. The canonical form **4b** may be an important contributor to the structure of 3-diazopropene, since the protons on the

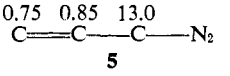


4a **4b**

γ-carbon appear at the unusually high field of τ 8.93.[10] This partial negative charge is undoubtedly reduced when cyclization occurs (compare the asterisked carbons in **1**, **2**, and **3**). Thus the amount of negative charge on the γ-carbon must be reduced in the transition state, and the reaction is favored, albeit only weakly, be electron-donating groups on the γ-carbon.

Conjugation in the dipolarophile increases its reactivity in 1,3-dipolar cycloadditions.[9a,b] Thus styrene is 20 times more reactive toward diphenyldiazomethane than are aliphatic alkenes. This rate enhancement has been ascribed to two factors:[9b] (1) the polarizability of the π electrons is increased, resulting in a greater tendency to enter into cyclic electron shifts; (2) unequal progress of bond formation in the transition state may result in small partial charges which can be stabilized through conjugation. The favorable effect of aryl substitution on the rate of cyclization of diazoalkenes to pyrazoles can be seen from the data in Table II. Substitution of a phenyl ring for a 1-hydrogen in 3-diazopropene increased the reaction rate by a factor of 6.

The most pronounced structural effect on the cyclization rate involves the difference between primary and secondary diazoalkenes. Thus β- and γ-methyl substituents have almost no effect on the cyclization rate of 3-diazopropene, whereas α substitution has a marked accelerating effect. Formula **5** shows the relative



5

rates of the three methyl compounds, compared to 3-diazopropene itself.

It is well known that α-electron-withdrawing groups stabilize diazoalkanes, whereas electron-donating substituents have the opposite effect. Presumably due to the carbanionic character of the α-carbon, secondary diazoalkanes are appreciably less stable than primary diazoalkanes. Thus the greater reactivity of 3-diazo-1-butene over 3-diazopropene in the cyclization reaction may simply reflect the higher ground-state energy of the secondary diazoalkene.

To summarize, the small ρ value for the cyclization of 1-aryl-3-diazopropenes, the rate enhancement by aryl conjugation with the carbon–carbon double bond, and the relative insensitivity of the reaction rate to structural changes all support the conclusion that cyclization of 3-diazoalkenes to pyrazoles is an intramolecular, concerted 1,3-dipolar cycloaddition.

Experimental Section

General. Unless otherwise specified, all melting points and boiling points are uncorrected. Elemental analyses were carried out by Spang Microanalytical Laboratories, Ann Arbor, Mich. Spectrometers used were the Varian A-60 (nmr), Unicam SP200 (ir), and Unicam SP800 or Beckman DB (visible, uv). All spectra were calibrated against standard references.

Ethyl Allylcarbamate. Ethyl chloroformate (109 g, 1.0 mol) was added dropwise to a well-stirred solution of 51 g (1.0 mol) of allylamine in 500 ml of anhydrous ether at 10°. A solution of 40 g (1.0 mol) of sodium hydroxide in 100 ml of water was slowly added simultaneously with the second half of the ethyl chloroformate. The mixture was stirred for 1 hr after the addition was complete and the two phases were separated. The ether layer was washed with 1 *N* hydrochloric acid and water, then dried ($MgSO_4$), concentrated, and distilled giving 103 g (91%) of a clear, colorless liquid, bp 111–114° (50 mm) (lit.[11] bp 194.5–195° (768 mm)).

N-(2-Methyl-2-propenyl)phthalimide. A slurry of 70 g (0.76 mol) of 3-chloro-2-methylpropene and 154 g (0.80 mol) of potassium phthalimide in 300 ml of dimethylformamide was heated at 155° for 2 hr, then cooled and poured into 400 ml of cold water. The solid which separated was recrystallized from 300 ml of ethanol. The purified product, 111 g (72%), had the following properties: white crystals, mp 87–88° (lit.[12] mp 88.5–90°).

Ethyl 2-Methyl-2-propenylcarbamate. A solution of 109 g

(10) A. Ledwith and E. C. Friedrich, *J. Chem. Soc.*, 504 (1964).

(11) S. Nirdlinger and S. F. Acree, *Am. Chem. J.*, **43**, 358 (1910).

(12) R. Adams and T. L. Cairns, *J. Am. Chem. Soc.*, **61**, 2464 (1939).

(0.55 mol) of N-(2-methyl-2-propenyl)phthalimide and 30 g (0.60 mol) of 99% hydrazine hydrate in 350 ml of ethanol was refluxed for 4 hr. The resulting thick white slurry was cooled, and 51 ml (0.60 mol) of concentrated HCl was added. The slurry was filtered and the phthalhydrazide which separated was washed with water (two 150-ml portions). The combined filtrate was evaporated to dryness under vacuum. The residue was dissolved in 50 ml of water, and the solution was made basic by slowly adding 26 g (0.65 mol) of sodium hydroxide dissolved in 50 ml of water. Then it was extracted with ether (four 100-ml portions) and the combined extracts were dried ($MgSO_4$). The carbamate of 3-amino-2-methylpropene was prepared directly from this solution using the procedure described for the preparation of ethyl allylcarbamate. The product, 52 g (67%), had the following properties: colorless liquid, bp 104–106° (22 mm); ir (CCl_4) 3490, 2990, 1721, 1657, 1515, 1218, and 905 cm^{-1}; nmr (CCl_4) τ 8.83 (t, 3, J = 7 Hz), 8.30 (s, 3), 6.33 (d, 2, J = 6 Hz), 5.92 (q, 2, J = 7 Hz), 5.19 (m, 2), and 3.96 (broad singlet, 1).

Anal. Calcd for $C_7H_{13}NO_2$: C, 58.72; H, 9.15; N, 9.78. Found: C, 58.66; H, 9.19; N, 9.72.

Substituted N-(*trans*-3-Phenyl-2-propenyl)phthalimides. The *m*-nitro-, *p*-chloro-, and *p*-methyl-substituted phthalimides were prepared from the corresponding substituted *trans*-3-chloro-1-phenylpropenes[13] using the following procedure. A slurry of 0.15 mol of the allylic chloride and 0.17 mol of potassium phthalimide in 550 ml of dimethylformamide was stirred at 25° for 16 hr. The slurry was poured into 1 l. of cold water. The solid that precipitated was separated by filtration, washed with water, and air dried. The properties and yields of these products are listed below.

N-[*trans*-3-(*m*-Nitrophenyl)-2-propenyl]phthalimide: yield 100%; light yellow crystals from acetone, mp 153.3–153.8°; ir (CCl_4) 2930, 1715, 1538, 1390, 1350, 970, and 960 cm^{-1}.

Anal. Calcd for $C_{17}H_{12}N_2O_4$: C, 66.23; H, 3.92; N, 9.09. Found: C, 66.18; H, 3.95; N, 9.12.

N-[*trans*-3-(*p*-Chlorophenyl)-2-propenyl]phthalimide: yield 81%; white crystals from benzene, mp 171.5–172.5°; ir ($CHCl_3$) 1768, 1710, 1405, 1105, and 980 cm^{-1}; nmr ($DCCl_3$) τ 5.59 (d, 2, J = 5.6 Hz), 4.09–3.25 (2, AB quartet, J = 15.4 Hz, with the high-field doublet split into two triplets, J = 5.6 Hz), 2.80 (s, 4), and 2.23 (m, 4).

Anal. Calcd for $C_{17}H_{12}ClNO_2$: C, 68.58; H, 4.04; N, 4.71. Found: C, 68.62; H, 4.03; N, 4.72.

N-[*trans*-3-(*p*-Tolyl)-2-propenyl]phthalimide: yield 98%; mp 165–166°; ir (CCl_4) 1770, 1720, 1430, 1395, and 1350 cm^{-1}; nmr ($DCCl_3$) τ 7.74 (s, 3), 5.60 (d, 2, J = 5.7 Hz), 4.20–3.30 (2, AB quartet, J = 15.4 Hz, with the high-field doublet split into two triplets, J = 5.6 Hz), 2.87 (AB quartet, 4, J = 8.8 Hz), and 2.27 (m, 4).

Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 78.06; H, 5.43; N, 4.97.

Hydrochloride of Substituted *trans*-3-Amino-1-phenylpropenes. A solution of 0.15 mol of the appropriate N-(*trans*-3-aryl-2-propenyl)phthalimide and 0.30 mol of 99% hydrazine hydrate in 500 ml of methanol was refluxed for 4.5 hr. The slurry was cooled, diluted with 250 ml of concentrated hydrochloric acid, and again refluxed for 30 min. After being cooled, the slurry was filtered and the solid phthalhydrazide collected was washed with 200 ml of water. The methanol and a portion of the water was distilled from the combined filtrates at 60° and slightly reduced pressure. When the residue was cooled in ice, solid amine hydrochloride precipitated. The yields and properties of these compounds are listed below.

Hydrochloride of *trans*-3-amino-1-(*m*-nitrophenyl)propene: yield 96%; cream-colored solid, mp 180–182° dec; ir (KBr) 3400–2500 (very broad band), 1535, 1500, 1350, 1100, 970, 810, and 730 cm^{-1}.

Hydrochloride of *trans*-3-amino-1-(*p*-chlorophenyl)propene: yield 70%; white plates from water, corrected mp 241–251°.

Hydrochloride of *trans*-3-amino-1-(*p*-tolyl)propene: yield 79%; white crystals from water, corrected mp 236–239°.

The hydrochloride of *trans*-3-amino-1-phenylpropene was prepared using the procedure described by Gensler and Rockett.[14]

Ethyl *trans*-3-Aryl-2-propenylcarbamates. A solution of 0.25 mol of the appropriate amine hydrochloride in 200 ml of water was made basic by slowly adding 0.37 mol of sodium hydroxide dissolved in 50 ml of water. The mixture was extracted with ether (three 50-ml portions) and the combined extracts were dried ($MgSO_4$). The ethyl carbamates were prepared from these amine solutions using the procedure described for the preparation of ethyl allylcarbamate. The crude products were purified by recrystallization. The yields and properties of these products are as follows.

Ethyl *trans*-3-(*m*-nitrophenyl)-2-propenylcarbamate: yield 52%; white needles from ether, mp 92.0–92.5°; ir (CCl_4) 3490, 3000, 2950, 1720, 1535, 1510, 1222, and 970 cm^{-1}; nmr (acetone) τ 8.78 (t, 3, J = 6.8 Hz), 5.89 (4, quartet, J = 6.8 Hz, overlapping a doublet, J = 6 Hz, centered at τ 6.02 in which both lines are further split into doublets, J = 4.2 Hz), 3.90–3.13 (3, AB quartet, J = 16.0 Hz, in which the high-field doublet is further split into two triplets, J = 4.2 Hz, and which is superimposed on a very broad singlet at τ 3.60), and 2.63–1.80 (m, 4).

Anal. Calcd for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.71; H, 5.58; N, 11.12.

Ethyl *trans*-3-(*p*-chlorophenyl)-2-propenylcarbamate: yield 52%; white blades from hexane, mp 89.0–89.5°; ir (CCl_4) 3490, 3000, 1703, 1510, 1220, 1090, and 975 cm^{-1}; nmr ($DCCl_3$) τ 8.77 (t, 3, J = 7.1 Hz), 6.10 (4, triplet, J = 5.0 Hz, overlapping a quartet, J = 7.1 Hz centered at τ 5.86), 4.79 (broad singlet, 1), 4.15–3.40 (2, AB quartet, J = 15.9 Hz, with the high-field doublet split into two triplets, J = 5.0 Hz), and 2.80 (s, 4).

Anal. Calcd for $C_{12}H_{14}ClNO_2$: C, 60.06; H, 5.89; N, 5.84. Found: C, 60.02; H, 6.02; N, 5.86.

Ethyl *trans*-3-phenyl-2-propenylcarbamate: yield 85%; white crystals from hexane, mp 52.5–53.5°; ir (CCl_4) 3497, 2998, 1720, 1506, 1225, 970, and 695 cm^{-1}; nmr (CCl_4) τ 8.82 (t, 3, J = 7.2 Hz), 6.17 (4, a triplet, J = 5.5 Hz, overlapping a quartet, J = 7.2 Hz, centered at τ 5.96), 4.45 (very broad singlet, 1), 4.29–3.39 (2, AB quartet, J = 16 Hz, with the high-field doublet split into two triplets, J = 5.5 Hz), and 2.78 (s, 5).

Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.09; H, 7.32; N, 6.82.

Ethyl *trans*-3-(*p*-tolyl)-2-propenylcarbamate: yield 85%; white crystals from hexane, mp 61.5–62.5°; ir (CCl_4) 3475, 2980, 1720, 1505, and 1220 cm^{-1}; nmr (CCl_4) τ 8.85 (t, 3, J = 7.1 Hz), 7.75 (s, 3), 6.22 (4, triplet, J = 5.5 Hz, overlapping with a quartet, J = 7.1 Hz, centered at τ 5.97), 4.47 (broad singlet, 1), 4.27–3.44 (2, AB quartet, J = 15.6 Hz, with the high-field doublet split into two triplets, J = 5.5 Hz), and 2.95 (4, AB quartet, J = 8 Hz).

Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.82; N, 6.39. Found: C, 71.11; H, 7.76; N, 6.31.

Aliphatic Ethyl Alkenylnitrosocarbamates. Ethyl *trans*-2-butenylcarbamate and ethyl 1-methyl-2-propenylcarbamate were prepared as described elsewhere.[5] A cold solution of 0.12 mol of dinitrogen tetroxide[15] in 60 ml of anhydrous ether was added to a solution of 0.12 mol of the appropriate ethyl alkenylcarbamate in 60 ml of anhydrous ether at −50°. The blue solution was stirred under nitrogen and was allowed to warm to 10°. The resulting yellow solution was washed with 5% sodium bicarbonate and water and then dried ($MgSO_4$). The ether was removed at reduced pressure leaving a yellow, liquid product. The yields and properties of these nitrosocarbamates are given below.

Ethyl allylnitrosocarbamate:[8] yield 91%; ir (CCl_4) 3000, 1741, 1648, 1513, and 1132 cm^{-1}; nmr (neat) τ 8.66 (t, 3, J = 7 Hz), 5.47 (4, a doublet, J = 5 Hz, which is more finely split and which is overlapping with a quartet, J = 7 Hz, centered at τ 5.47), and 5.47–4.0 (m, 3).

Ethyl 2-methyl-2-propenylcarbamate: yield 93%; ir (CCl_4) 2990, 1742, 1660, 1530, 1422, 1390, 1358, 1150, 1090, and 820 cm^{-1}; nmr (CCl_4) τ 8.55 (t, 3, J = 7 Hz), 8.35 (s, 3), 5.73 (s, 2), and 5.50 (6, a quartet, J = 7 Hz, superimposed on two multiplets centered at τ 5.50 and 5.24).

Aromatic Ethyl Alkenylnitrosocarbamates. A cold solution of 2.9 g (44 mmol) of nitrosyl chloride[15] in 6 ml of dry pyridine was slowly added to a stirred solution of 20 mmol of the appropriate ethyl *trans*-3-aryl-2-propenylcarbamate in 30 ml of dry pyridine at −5° under a nitrogen atmosphere. Pyridine hydrochloride precipitated. The slurry was stirred for 15 min, then poured into 300 ml of water. The yellow oil which separated was taken up in ether. The solution was washed successively with 1 *N* hydrochloric acid, water, and 5% sodium bicarbonate. After the solution was dried ($MgSO_4$), the ether was removed at reduced pressure leaving the crude product. The preparation of the *p*-methyl-substituted compound was run at −20° using a 1:1 mole ratio of nitrosyl chloride

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to carbamate and the crude product was purified by elution from a column of silica gel (200 g) with 1:1 hexane–benzene. The desired nitrosocarbamate was the first material to elute. The other crude nitrosocarbamates were fairly pure. The liquid products were used without further purification, but the solids were recrystallized. The yields and properties of these compounds are listed below.

Ethyl *trans*-3-(*m*-nitrophenyl)-2-propenylnitrosocarbamate: yield 97%; yellow crystals from cyclohexene, mp 69.5–70.5°; ir (CCl_4) 2990, 1740, 1535, 1350, 1140, and 970 cm^{-1}; nmr ($DCCl_3$) τ 8.52 (t, 3, J = 7.2 Hz), 5.47 (4, doublet, J = 5.5 Hz, which overlaps a quartet, J = 7.2 Hz, centered at τ 5.44), 4.19–3.25 (2, an AB quartet, J = 15.8 Hz, in which the high-field doublet is split into two triplets, J = 5.5 Hz), and 2.71–1.80 (m, 4).

Ethyl *trans*-3-(*p*-chlorophenyl)-2-propenylnitrosocarbamate: yield 97%; yellow crystals from methanol–water, mp 57.5–58.5°; ir (CCl_4) 2990, 1740, 1520, 1410, 1380, 1350, 1140, 1090, and 920 cm^{-1}; nmr (CCl_4) τ 8.57 (t, 3, J = 7.3 Hz), 5.63 (4, doublet, J = 5.9 Hz, overlapping a quartet, J = 7.3 Hz, centered at τ 5.52), 4.44–3.44 (2, AB quartet, J = 15.6 Hz, in which the high-field doublet is split into two triplets, J = 5.9 Hz), and 2.84 (s, 4).

Ethyl *trans*-3-phenyl-2-propenylnitrosocarbamate: yield 94%; yellow liquid; ir (CCl_4) 2995, 1740, 1521, 1380, 1136, and 925 cm^{-1}; nmr (CCl_4) τ 8.68 (t, 3, J = 7.2 Hz), 5.57 (4, doublet, J = 5.6 Hz, superimposed on a quartet, J = 7.2 Hz, centered at τ 5.57), 4.30–3.25 (2, an AB quartet, J = 15.8 Hz, with the high-field doublet split into two triplets, J = 5.6 Hz), and 2.80 (s, 5).

Ethyl *trans*-3-(*p*-tolyl)-2-propenylnitrosocarbamate: yield 43%; yellow crystals from hexane, mp 44.5–45.0°; ir (CCl_4) 3000, 1740, 1520, 1420, 1380, 1350, 1140, and 930 cm^{-1}; nmr (CCl_4) τ 8.62 (t, 3, J = 7 Hz), 7.75 (s, 3), 5.65 (4, a doublet, J = 6.1 Hz, superimposed on a quartet, J = 7 Hz, centered at τ 5.55), 4.47–3.39 (2, an AB quartet, J = 15.8 Hz, with the high-field doublet split into two triplets, J = 6.1 Hz), and 2.95 (AB quartet, 4, J = 7 Hz).

3-Diazoalkenes. A solution of 10 mmol of the appropriate ethyl alkenylnitrosocarbamate in 20 ml of cyclohexene was slowly added to a mixture of 30 ml of cyclohexene and 10 ml of 3 *N* methanolic sodium methoxide. The mixture was stirred in the dark at +4° for 1.5 hr for all preparations except those of 3-diazo-1-butene and *trans*-3-diazo-1-(*p*-chlorophenyl)propene. In these preparations stirring times were 0.5 and 2.5 hr, respectively. The mixture was extracted twice with cold, dilute sodium hydroxide, and the red cyclohexene solution of diazo compound was dried briefly over potassium hydroxide pellets at 4°. The yields and some spectroscopic data of these diazo compounds are shown in Table I. The yields were determined by measuring the volume of gas evolved when a sample of the solution was added to a solution of *p*-nitrobenzoic acid in diglyme.

Pyrazoles. A red solution of 3-diazoalkene in cyclohexene was allowed to stand at room temperature in the dark for 48 hr. The red color disappeared. The pyrazole was isolated from the solution as described below. The yield of pyrazole based on the 3-diazoalkene was determined in a separate experiment by measuring the concentration of diazo compound in the starting solution spectroscopically. At the same time several drops of acetic acid were added to a sample of the solution to destroy the diazo compound present. A second sample of the solution was allowed to stand until all the 3-diazoalkene had cyclized. The increase in pyrazole content of the second sample in comparison to that of the first sample was used to calculate the yield. The analyses for pyrazole and the methyl-substituted pyrazoles were carried out by glpc using hexamethylbenzene as an internal standard. The analyses were performed on a 5-ft Carbowax 20M column at 215° with a helium flow rate of 40 cc/min. The analyses for the phenyl-substituted pyrazoles were carried out by extracting these pyrazoles from the cyclohexene solutions with 3 *N* hydrochloric acid and by measuring the pyrazole content of these extracts by uv spectroscopy.

Pyrazole was obtained from 3-diazopropene in 100% yield. The reaction solution was concentrated to 3 ml and 10 ml of hexane was added. White needles, mp 68–70° (lit.[17] mp 70°), were obtained when the crude product that precipitated was sublimed. The ir and nmr spectra of this material were identical with those of an authentic sample of pyrazole.

3(5)-Methylpyrazole was obtained from both *trans*-1-diazo-2-butene (109%) and 3-diazo-1-butene (yield not determined). The liquid produced was isolated from the reaction mixture by glpc using the conditions described above. Its infrared and nuclear magnetic resonance spectra were identical with the reported spectra of 3(5)-methylpyrazole.[18,19]

4-Methylpyrazole was obtained (100%) from 3-diazo-2-methylpropene. It was isolated from the residue remaining after the cyclohexene was distilled from the reaction mixture by glpc under the conditions described above. The nmr spectrum of this liquid was identical with that reported in the literature.[18] Its picrate was prepared, mp 140–141° (lit.[20] mp 142°).

The four phenyl-substituted pyrazoles were isolated in crude form by extracting the reaction mixtures with 3 *N* hydrochloric acid. The combined extracts were made basic by adding solid potassium carbonate. The organic material which separated was taken up in ether, the ether was dried ($MgSO_4$), and the solution evaporated to dryness leaving the crude pyrazole.

The crude 3(5)-(*m*-nitrophenyl)pyrazole obtained (89%) from *trans*-3-diazo-1-(*m*-nitrophenyl)propene was recrystallized from benzene–hexane and sublimed at 150° (1 mm) to give white crystals: mp 121.0–121.7° (lit.[21] mp 120°); uv max (3 *N* HCl) 250 mμ (ϵ 2.46 × 10^4); ir (KBr) 3490, 3190, 2950, 1535, 1350, 780, and 745 cm^{-1}; nmr (acetone) τ 3.15 (d, 1, J = 2.5 Hz) 2.16 (d, 1 J = 2.5 Hz), 2.56–1.20 (m, 4), and −1.30 (very broad singlet, 1).

3(5)-(*p*-Chlorophenyl)pyrazole obtained (87%) from *trans*-3-diazo-1-(*p*-chlorophenyl)pyrazole was recrystallized from hexane to give fluffy white crystals: mp 96–97° (lit.[21] mp 98°); uv max (3 *N* HCl) 259 mμ (ϵ 2.14 × 10^4); ir (CCl_4) 3500, 3200, 2970, 1502, 1450, and 1095 cm^{-1}; nmr (CCl_4) τ 3.05 (broad singlet, 1), 2.63 (5, AB quartet, J = 9 Hz, superimposed on a singlet at τ 2.54), and −3.88 (s, 1).

3(5)-Phenylpyrazole obtained (86%) from *trans*-3-diazo-1-phenylpropene was recrystallized from 2:1 hexane–benzene to give white crystals: mp 72–73° (lit.[22] mp 78°); uv max (3 *N* HCl) 248 mμ (ϵ 1.42 × 10^4); ir (CCl_4) 3490, 3190, 2950, 1460, and 695 cm^{-1}; nmr (CCl_4) τ 3.95 (d, 1, J = 1.0 Hz), 2.61 (6, doublet, J = 1.0 Hz, superimposed on a multiplet extending from τ 2.81 to 2.35), and −4.02 (broad, singlet, 1).

The crude 3(5)-(*p*-tolyl)pyrazole obtained from *trans*-3-diazo-1-(*p*-tolyl)propene (yield not determined) was recrystallized from 4:1 hexane–benzene to give white crystals: mp 81.0–81.5° (lit.[23] mp 87–88); uv max (3 *N* HCl) 260 mμ (ϵ 1.90 × 10^4); ir (CCl_4) 3480, 3180, 2925, 1522, 1450, 1047, 958, and 935 cm^{-1}; nmr (CCl_4) τ 7.74 (s, 3), 3.62 (broad singlet, 1), 3.11–2.34 (5, AB quartet, J = 8 Hz, superimposed on a singlet at τ 2.50), and −3.92 (broad singlet, 1).

Rates of Cyclization. A cyclohexene solution of the 3-diazoalkene in a black bottle was equilibrated at 25.0° in a constant-temperature bath. The rate of disappearance of the diazoalkene was followed by observing the decrease absorbance with time. Plots of log ($A - A_\infty$) *vs.* time were straight lines for all the compounds. Table II shows the first-order rate constants for these cyclizations. The wavelengths of light used to follow the reactions were the λ_{max} of the aliphatic 3-diazoalkenes (Table I) and 550 mμ for the aryl compounds.

Acknowledgment. We are indebted to the Graduate Council of Michigan State University and to the National Science Foundation for financial support of this work.

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