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Reaction of vinyl azides with nitrosyl tetrafluoroborate yields 1,2,5-oxadiazoles and 1,2,4-oxadiazoles depending on the structure of the azide. Reaction of 1,2-dialkyl vinyl azides with nitryl tetrafluoroborate gives 2-oxo-1,2,5-oxadiazoles in high yields whereas 1-aryl-2-alkyl vinyl azides gave moderate yields of 3-aryl-1,2,5-oxadiazoles and 5-aryl-1,2,4-oxadiazoles. Acyl chlorides condense with vinyl azides in the presence of aluminum chloride to yield oxazoles. Dimethyl acetylenedicarboxylate condenses with vinyl azides by cycloaddition of the azido function with the alkyne and by cycloaddition of the vinyl group with the alkyne. The latter process occurs only under the influence of AlCl₃. The observed reactions are viewed as involving the participation of vinyl azides as N-diazoenamines.

La réaction des azotures de vinyle sur le tétrafluoroborate de nitrosyle conduit aux oxadiazoles-1,2,5 et oxadiazoles-1,2,4 dépendant de la structure de l'azoture. La réaction des azotures de dialkyl-1,2 vinyle sur le tétrafluoroborate de nitryle mène aux oxo-2 oxadiazoles-1,2,5 avec des rendements élevés tandis que les azotures d'aryl-1 alkyl-2 vinyle conduisent aux aryl-3 oxadiazoles-1,2,5 et aryl-5 oxadiazoles-1,2,4. Les chlorures d'acyle se condensent aux azotures de vinyle en présence de chlorure d'aluminium pour donner des oxazoles. L'acétylène dicarboxylate de diméthyle se condense aux azotures de vinyle par cycloaddition de la fonction azoture sur l'alkyne et par cycloaddition du groupe vinyle sur l'alkyle. Cette dernière ne se produit qu'en présence de AlCl₃. Les réactions observées ont été examinées sous l'angle d'une participation des azotures de vinyle sous forme de N-diazoénamines.

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Introduction

The synthetic utility of enamines lies principally in their ability to react with electrophiles at the β -vinyl carbon and undergo cycloaddition at the carbon-carbon double bond (1). The ease of synthesis of the vinyl azide function (2), coupled with HMO calculations (3) and spectral characteristics (3, 4), which indicate there is appreciable electron density at the β -vinyl carbon, make this functional group a logical choice for reaction with electrophiles. The reactions of vinyl azides with acids produce amides via a route most easily rationalized as occurring via protonation of the β -vinyl carbon (5). Reactions with halogens lead to α -haloketones by similar involvement of the β -vinyl carbon (6). The recently reported (7) reactions of vinyl azides with diphenylketene revealed similar nucleophilic behavior of the β -vinyl carbon (see Scheme 1). This latter process may be considered a member of a general class of reactions in which the azide participates as an N-diazoenamine.

We have found that vinyl azides react readily with several electrophilic reagents to yield products expected to result from this and closely related transformations (see Scheme 2).

Results and Discussion

Reaction of nitrosyl tetrafluoroborate (NOBF₄) with vinyl azides in cold (-15°) acetonitrile results in smooth evolution of nitrogen and production of 1,2,5-oxadiazoles and 1,2,4-oxadiazoles, depending on the structure of the azide. Thus, reaction with 1,2dialkyl substituted vinyl azides (1a-c) for short periods (30 min -1 h) followed by addition of water and separation of the organic products gave moderate yields of 1,2,5-oxadiazoles (2a, b)(8) and lesser amounts of amides (3a-c). When the reactions were allowed to proceed for extended periods (18 h) the yields of oxadiazoles increased to near 80% while those of the amides decreased to less than 10%. The decreased yields of amides upon prolonged reaction time suggests these products arise from hydrolysis of the azides promoted by the acid (5) (HBF₄) presumably generated during oxadiazole formation.

Reaction of the *trans*-1-azido-1-phenylpropene

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(1d) with NOBF₄ gave, in addition to the expected 1,2,5-oxadiazole (2c) a comparable amount of 1,2,4-oxadiazole (4a) considered to be formed as shown in Scheme 3. The proposed route to 4 was supported by the detection of benzonitrile in the reaction mixture.

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Reactions of 2-alkyl substituted vinyl azides such as 1e with NOBF₄ gave moderate yields of amides. No evidence for synthetically useful yields of heterocyclic products was obtained.

Reaction of 1,2-dialkyl substituted vinyl azides (1*a*, *b*) with nitryl tetrafluoroborate (NO₂BF₄) gave high yields of 2-oxo-1,2,5-oxadiazole (5, Scheme 4). Extension of this reaction to the 1-aryl-2-alkyl substituted 1*d* gave N₂O, 1,2,5-oxadiazole (2*c*), 1,2,4-oxadiazole (4*a*), and benzonitrile. The latter three products were formed in similar proportions to that observed in the reaction of NOBF₄ with this azide. In a similar manner reaction of α -azidostyrene (1*f*) with NO₂BF₄ gave 2*d* and 4*b*. As was the case with reaction with NOBF₄, the reaction of 2-alkyl substituted vinyl azides (1*e*) with NO₂BF₄ did not give synthetically useful yields of heterocyclic products.

We consider the mechanism most consistent with these observations to be that depicted in Scheme 4, where both the $NOBF_4$ and NO_2BF_4 reactions proceed via a common intermediate, 6. It is noteworthy that 1d gives only the product 4a of alkyl migration of intermediate 6. Protonation of 1d has been reported (5) to yield amides 3d and e in a ratio of 0.6:1. Since the latter is considered to be the product of phenyl migration in an intermediate resembling 6, we expected a product arising from this migration to be present in this reaction. The formal product of phenyl migration in this case would be an α oximino amide or conceivably an α -keto amido. A v.p.c./mass spectral analysis of the reaction mixture failed to detect a product with a molecular weight corresponding to either of these possibilities.

In an effort to extend the reactions of NO⁺ and NO₂⁺ with vinyl azides to other electrophiles we studied their reactions with acyl chlorides under a variety of conditions. Reaction of acetyl chloride with 1*a* and *b* at room temperature resulted in evolution of nitrogen and gave, on hydrolytic work, amides 3*a* and *b* as the only identifiable products. In the presence of aluminum chloride the same reaction proceeded with evolution of nitrogen to give a 70% yield of 2,3,5-trimethyl oxazole, 7.

Although we have not investigated appropriately substituted acyl chlorides which enable one to differentiate the several attractive mechanisms that may be envisioned for the production

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 $5 R = R' = CH_3$

SCHEME 4. Reaction of vinyl azides with NO₂BF₄.



of oxazole products from this reaction, we have investigated the reaction of 1-azido-1-phenylpropene (1d) with acetyl chloride. This reaction yielded oxazoles 8, 9, and 10 in 17, 7, and 1%yields respectively. These products may be envisioned as being formed by several alternate mechanisms (Scheme 5). Fowler and Hassner (8) have previously demonstrated that reaction of benzoyl chloride with 2-phenyl-3-methyl azirine gives 2,5-diphenyl-4-methyl oxazole (analogous to 8) via an N-benzoyl chloroaziridine.¹

Thermal (room temperature $\rightarrow 80$ °C) reactions of ketene dimer, phenyl isocyanate, benzyl chloride, methyl iodide, cyclohexanone, carbon disulfide, methyl chloroformate, and benzenediazonium tetrafluoroborate with vinyl azides 1*a* and *b* did not produce synthetically useful yields of heterocyclic products. Indeed reactions with these potential electrophiles in several solvents (CH₃CN, (C₂H₅)₂O, C₆H₆) with and without added aluminum chloride lead to reactions with solvent (*e.g.* phenylacetamide from benzenediazonium tetrafluoroborate and acetonitrile) and conversion of azides to amides upon hydrolytic work-up.

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Since enamines readily undergo cycloaddition reactions with dipolarophilic reagents, we explored the reaction of dimethyl acetylene dicarboxylate (DMAD) with azides 1a and b. Depending on the reaction conditions either 1:1 or 2:1 DMAD:azide adducts were obtained. Reaction of 1b with DMAD at room temperature for 3 days gave triazole 11 (Scheme 6), whose n.m.r. spectrum was unambiguous. In addition to two methoxyl resonances (δ 3.98), two vinyl methyl resonances (one at δ 1.41 appearing as a quartet of quartets (J = 3.5, 0.5 Hz) and a second at 2.19 appearing as a

 ${}^{1}A$ referee has suggested that 8 and 10 could easily be explained by involvement of the antiaromatic *N*-acetyl-2-azirine, i.



quintet (J = 0.5 Hz)) were evident. A vinyl hydrogen appeared as a quartet of quartets J =3.5, 0.5 Hz at δ 5.83. This pattern is characteristic of the *trans*-vinyl system of the starting azide 1b (4, 5).

This reaction could be catalyzed by addition of aluminum chloride (1 h) but resulted in a significantly lower yield (90 vs. 55%) and with formation of a second product (16%). This second product possessed a molecular weight and elemental analysis corresponding to the addition of 2 mol of DMAD to 1 mol of the vinyl azide. It was observed that both azides 1aand b gave this product in comparable yields. Thus the stereochemistry of the vinyl group is inconsequential or destroyed during this reaction. This 2:1 adduct was the major (55%) product when the reaction was performed by addition of azide to a solution containing a two-fold or greater excess of DMAD and an equivalent of aluminum chloride. It was shown that the 1:1 adduct (11) could not be induced to react further with DMAD in the presence of aluminum chloride, thus it is not a precursor of the 2:1 adduct.

The n.m.r. spectrum of the 2:1 adduct revealed four distinct methoxyl groups, a methyl singlet (δ 2.03), a methyl doublet (δ 0.95, J = 7Hz), and a methine quartet (δ 3.28). Although both structures 12 and 13 (Scheme 6) are reasonable formulations for the 2:1 adduct based on mechanistic arguments and are consistent with elemental analysis and n.m.r. data, the pyrolytic conversion of the adduct to vinylic products indicates 12 is correct. Thus heating the adduct to 170° produced a mixture of two isomers, the major of which exhibited an n.m.r. spectrum which possessed, in addition to four methoxyl signals, a vinyl methyl singlet (δ 2.84), a vinyl methyl doublet (δ 1.72, J = 7 Hz), and a vinyl hydrogen quartet (δ 6.88, J = 7 Hz). The n.m.r. spectrum of the minor pyrolysis product also contained four methoxyl signals, a vinyl methyl singlet (δ 2.75), a vinyl methyl doublet (δ 1.91, J = 7 Hz), and a vinyl hydrogen quartet (δ 6.20, J = 7 Hz). This observation is compatible with a cyclobutene \rightarrow butadiene conversion and thus most consistent with 12 as the initial adduct. A priori four products (14-17) could be expected from 12 of undefined stereochemistry. The doublet resonance of the terminal vinyl methyl group (δ 1.72) of the major pyrolysis

CAN. J. CHEM. VOL. 51, 1973 C₆H₅ C-CH₃ CH₃ 8 C1 C₆H₅ 0 C-CH₃ CH₃ н C₆H₅ CI C₆H₅ 0 0 C_6H_5 Ш CH₃C-CI CH₃ AICI₃ CH3 CH3 CH_3 н 1d ⊕ -N₂ C_6H_5 C₆H₅ C_6H_5 C₆H₅ -. N N CH₃ 0 CH3 CH3 CH₃ C-CH3 CH-`СН₃ <u>9</u> C₆H₅

SCHEME 5. Reaction of 1-azido-1-phenylpropene with acetyl chloride.

product is at higher field than the same group of the minor product. This observation allows assignment of a *trans* relationship to this methyl and its vicinal carbomethoxy neighbor in the major isomer and a *cis* relationship in the minor isomer (9).

CH₃

CH₃

10

Comparison of the relative chemical shifts of the vinyl hydrogens associated with the carbons containing these terminal methyls confirms this assignment. The relative stereochemistry of the quaternary methyl and vicinal carbomethoxy about the nitrogen bearing double bonds of the

dienic pyrolysis product was deduced by inspection of the chemical shifts of the resonances due to the quaternary methyls. The signal due to this group was at higher field in the major isomer than in the minor isomers. This indicates the quaternary methyl and carbomethoxy function are *cis* to each other in the major isomer and have a *trans* relationship in the minor isomer (9). The major pyrolysis product is thus 14 and the minor product is 15. Since these two products interconvert thermally under the pyrolysis conditions they would probably inter-

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convert with 16 and 17. Thus, although the stereochemistry of 12 implied by these results is as shown it cannot be assigned with certainty. As noted above both 1a and b gave 12 in the aluminum chloride catalyzed addition of DMAD to the olefinic linkage of the vinyl azide. In both reactions a triazole was formed. In the case of reaction of 1b triazole 11 was formed whereas reaction of 1a gave the triazole isomeric with 11 about the olefinic linkage. This suggests the catalyzed addition of DMAD to the olefinic linkage. This suggests the catalyzed addition of DMAD to the olefinic bond of the vinyl azide is stepwise. This addition must be the initial reaction in the formation of the 2:1 adduct since the triazoles (11) are not converted to 12 under the reaction conditions.

It can be seen from the above examples that vinyl azides are potentially useful synthetic intermediates when viewed as *N*-diazoenamines.

Experimental

Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. I.r. spectra were recorded with a Perkin-Elmer 457 grating spectrometer. U.v. spectra were recorded on a Unicam SP800 spectrometer. N.m.r. spectra were obtained with Varian A 56/60 and HX100 Spectrometers using tetramethylsilane as an internal standard ($\delta = 0$). Mass spectra were obtained using a Hitachi-Perkin-Elmer RMU6E Spectrometer and an ionization voltage of 80 eV.

Reaction of 1a and b with NOBF₄

To a solution of 1*a* or *b* (10) (1 g, 10.3 mmol) in 10 ml acetonitrile at 0° under He was added 1.2 g (20 mmol) NOBF₄ over 30 min, nitrogen (mass spectra) evolution was immediate. After 1 h of further stirring the reaction was quenched with water and extracted with three 100-ml portions of ether. The solvent was removed by fractional distillation and the residue fractionated at 20 mm (65°) to yield 0.70 g (~68%) of 3,4-dimethyl-1,2,5-oxadiazole (2*a*, lit. (11) b.p. (760 mm) 155–156°) which was identified by comparison of its mass and n.m.r. spectra with those published (11) for this compound.

The undistilled residue (0.3 g) was chromatographed on 20 g SiO₂. Initial elution with benzene-methanol (99:1 v/v) gave 0.2 g (19%) of *N*-ethyl acetamide (3*a*) (5). Continued elution with this solvent system gave 0.1 g (9%) *N*-methyl propionamides (3*b*) (5). Both amides gave expected i.r., n.m.r., and mass spectra.

This experiment was repeated using 1 g of 1a or b and allowing the reaction to proceed for 30 min. After this time one-half of the reaction mixture was removed, diluted with water, and extracted $(3 \times 100 \text{ ml})$ with ether. The ethereal extract was concentrated and analyzed by g.l.p.c. (15% Versamide 900 on Chrom W, 3 ft × 1/8 in. column; temperature programmed 50–150° at 10°/min; using o-chlorotoluene as an internal standard) to yield (calcd.) 78–80% of 2a, 11% of 3a, and 6% of 3b. After 18 h the second half of the reaction was similarly analyzed to yield 92–94% of 2a, and 1% of a mixture of 3a and b.

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Reaction of 1c with NOBF₄

Reaction of 1*c* (1 g, 6.6 mmol) in 10 ml of acetonitrile at 0° under He with 0.89 g (7.6 mmol) of NOBF₄ for 1 h followed by the hydrolytic work-up described above gave organic products which were chromatographed on 20 g SiO₂. Elution with benzene gave 0.76 g (75%) of 3,4hexamethylene-1,2,5-oxadiazole (2*b*); v_{max} (film) 2920, 2860, 1450, 1180, 1010, and 930 cm⁻¹; λ_{max} (MeOH) 220 m μ (ϵ 2420); n.m.r. (CCl₄), δ 2.88 (4H J = 6 Hz, t) and 1.60 (8H, m).

Mol. wt. Calcd. for $C_8H_{12}N_1O$: 152.0949. Found $[M^+]$: 152.0959.

Continued elution with benzene-methanol (99:1) yielded 9% of lactam 3c, m.p. $72.5-73^{\circ}$ (lit. (12) m.p. $72-73^{\circ}$); v_{max} (KBr) 3280 and 1700 cm⁻¹.

Reaction of 1d with NOBF₄

To 0.556 g (3.5 mmol) of 1d in 15 ml acetonitrile at -10° under He was added a slurry of NOBF₄ (0.41 g, 3.1 mmol) in acetonitrile (30 ml). Nitrogen (mass spectra) evolution was immediate. After 18 h at room temperature the solution was quenched with water and extracted continuously with ether. Concentration of the extract gave a solution which was analyzed by g.l.p.c. (2% SE30 on Chrom G, 5 ft × 1/8 in., temperature programmed 50–170° at 6°/min). Reaction products 2c (8.8%), 4a (12%), and benzonitrile (6%) were identified by mixed injection of authentic samples and comparison of mass spectra obtained on preparatively isolated samples. Yields were calculated *vs.* added internal standard (nitrobenzene).

An authentic sample of 3-phenyl-4-methyl-1,2,5oxadiazole (2c) was prepared by reaction of 1-oxo-3methyl-4-phenyl-1,2,5-oxadiazole (13) with PCl₅ (14).

An authentic sample of 3-methyl-5-phenyl-1,2,4oxadiazole (4a) was prepared by the method of Eloy (15).

Reaction of 1e with NOBF₄

The reaction of 1*e* with NOBF₄ in acetonitrile was carried out as described above for 1*d*. After the usual hydrolytic work-up the reaction extract was analyzed by a g.l.p.c. (SE 30, temperature programmed 50-290° at 4°/min) mass spectral combination. The only products detectable in more than 5% amounts *vs*. an internal standard were amides (5) (~30%) derived from hydrolysis of the azides (M⁺ 115).

Reaction of 1a and b with NO₂BF₄

To 0.5 g (5.2 mmol) 1a or b in 20 ml of ether at -10 °C under He was added dropwise a solution of 0.68 g (5.5 mmol) NO₂BF₄ in 10 ml of ether. Nitrogen (mass spectra) evolution was immediate. The reaction was allowed to warm to room temperature and was stirred at this temperature for 1 h. After hydrolysis and ether extraction fractional distillation yielded 0.3 g (51%) of 5 (b.p. (16 mm) 100°) which gave a mass spectra identical to that published (11). Analysis of the nonvolatile portion by g.l.p.c. (Versamide 900) vs. an internal standard revealed 20% of a mixture of 3a and b. Repetition of the experiment for 18 h yielded 0.49 g (83%) of 5.

Reaction of 1d with NO₂BF₄

To the azide (0.5 g) in 10 ml acetonitrile at -10° under He was added a molar equivalent of NO₂BF₄ in the same solvent (20 ml). Upon addition gas evolution (N₂ and

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N₂O by mass spectral analysis) occurred. After addition (25 min) the solution was stirred at room temperature for 24 h then worked-up by addition of water, extraction with ether, and concentration of the extract. Product identification (2c (17%), 4a (24%), benzonitrile (5%)) was made by g.l.p.c./mass spectra analysis (SE 30 column) as described for the NOBF₄ 1d reaction. Although yields are lower than for reaction of 1a, b with NO₂BF₄ the alternate products corresponding to 5 and amides were not present. Authentic 5 (R = C₆H₅, R' = CH₃ and R = CH₃, R' = C₆H₅) (13) as well as amide hydrolysis products (5) were available for comparisons.

Reaction of 1f with NO₂BF₄

To a 15 ml solution of 1.15 g (8.6 mmol) NO₂BF₄ in acetonitrile at 0° under He was added 1.25 g (8.6 mmol) 1*f* in 12 ml acetonitrile. The solution was stirred at room temperature for 18 h and worked-up in the usual manner. Analysis of the organic products by g.l.p.c./mass spectra (SE 30) indicated two major components both of which possessed [M]⁺ 146. These were separated by preparative g.l.p.c. (SE 30) and identified as 2*d* (16) (8%) and 4*b* (17) (12.5%) by comparison of n.m.r. and mass spectra with literature values.

Reaction of 1a and b with Acetyl Chloride

To a solution of acetyl chloride (0.81 g, 10 mmol) in 10 ml of dry ether under He was added vinyl azide (1a or b), (1.0 g, 10.3 mmol) during 1 h. The evolution of nitrogen was smooth. After stirring for 8 h the reaction was quenched with 10% aqueous NaHCO₃. Continuous extraction with ether followed by solvent removal gave only amides 3a (5) and b (5) (g.l.p.c./mass spectra, Versamide 900).

Repetition of the above using 1.4 g (10.5 mmol) $AlCl_3$ in the initial ether solution gave, after work-up, 1.03 g (70%) of an oil. Distillation (b.p. (15 mm) 65°) of the oil gave 0.8 g (70%) of 2,4,5-trimethyl oxazole (7) identified by g.l.p.c., mass spectra and n.m.r. comparison with an authentic sample (18).

Reaction of 1d with Acetyl Chloride

To a solution of acetyl chloride (0.39 g, 5 mmol) in ether (8 ml) under He containing AlCl₃ (0.67 g, 5 mmol) was added 1d (0.8 g, 5 mmol). The solution was stirred for 2–18 h and worked-up in the usual manner. Analysis by g.l.p.c./mass spectra (5% DEGS on Chrom W, 6 ft × 1/8 in. column, 100° for 30 min, 100–180° at 3°/min) revealed 8 (17%), 9 (7%), 10 (~1%), and amides (3%). Comparison of preparatively g.l.p.c. isolated samples with authentic samples (8 (19), 9 (20), 10 (19), amides (5)) confirmed the identity of the products.

Reaction of 1a and b with DMAD

Uncatalyzed

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> An ether solution (20 ml) containing 0.5 g 1b (5.2 mmol) and 0.7 g DMAD (4.9 mmol) was stirred for 3 days. Concentration of the solution gave 0.99 g 90% of triazole 11 (b.p. (0.1 mm) 150°) v_{max} (KCl): 2930, 1735, 1550, 1450, 825, and 810 cm⁻¹.

> Mol. wt. Calcd. for $C_{10}H_{13}N_3O_4$: 239. Found (M⁺): 239.

AlCl₃ Catalyzed

To a solution of 1 g (7 mmol) DMAD and 0.95 g (7.1 mmol) AlCl₃ in 20 ml of ether was added 0.7 g

(7.1 mmol) of 1b. The reaction was stirred for 18 h then quenched with excess 10% aqueous NaHCO₃, extracted with ether and chromatographed on 20 g of SiO₂. Elution with petroleum ether gave 0.4 g (23.5%) 11. Elution with 95:5 petroleum ether : chloroform gave 0.30 g (13%) of 12, m.p. 98-99°. Repetition of this experiment using an excess of DMAD gave unreacted DMAD, no 11, and raised the yield of 12 to 15%.

The first experiment was repeated using reverse addition of reactants. Thus *trans*-2-azido-2-butene (1*b*, 0.5 g, 5.2 mmol) was dissolved in 20 ml of dry ether and the solution cooled to -20 °C. To this was added aluminum chloride (0.8 g) followed by dropwise addition of DMAD (0.7 g, 4.9 mmol). The mixture was warmed to room temperature and after stirring overnight it was diluted with aqueous 10% NaHCO₃ until it was weakly basic. Continuous extraction with ether gave 1.00 g of oil. Direct chromatography on 30 g of SiO₂ using 95:5 chloroform – petroleum ether as eluent gave 0.7 g (55%) of 11.

Similarly reaction of *cis*-2-azido-2-butene (2 g, 20.8 mmol) was added dropwise to a solution of 2.4 g of AlCl₃ and DMAD (2.5 g, 17.8 mmol) in 20 ml of ether. After the usual work-up the residual oil was chromatographed on 100 g of SiO₂. Elution with petroleum ether gave 0.9 g of the *cis*-isomer of triazole 11; v_{max} (KBr) 2930, 1735, 1550, 1450, 825, and 810 cm⁻¹; n.m.r. (CDCl₃): δ 5.85 (1H, quartet, J = 7 of quartet, J = 1 Hz), and 1.85 (3H, d, J = 7 of quartet, J = 1 Hz).

Mol. Wt. Calcd. for $C_{10}H_{13}N_{3}O_{4}$: 239. Found (M⁺): 239.

Elution with 95:5 petroleum ether – chloroform gave 0.2 g (3%) of 12.

Anal. Calcd. for $C_{16}H_{19}N_3O_8$ ([M⁺] 381): C, 50.39; H, 4.99. Found (381): C, 50.52; H, 5.02.

Reaction of 11 with DMAD in the presence of AlCl₃

To a solution of 0.1 g of 11 in 5 ml of ether containing 0.1 g AlCl₃ was added 0.2 g DMAD. The reaction was stirred overnight at room temperature then quenched with aqueous 10% NaHCO₃. The mixture was continuously extracted with ether which was concentrated. The residue was chromatographed on 20 g SiO₂. Using petroleum ether as the eluent 0.18 g DMAD was recovered. Using 95:5 petroleum ether – chloroform as the eluent 0.08 g of 11 was recovered. T.l.c. analysis of the fractions which would contain 12 revealed its absence.

Pyrolysis of 12

A solution of (0.038 g) of 12 in 0.4 ml of nitrobenzene was heated in an n.m.r. tube at 165° for 3 h. The signals due to 12 disappeared and signals attributable of 14 and 15 appeared. Integration of the spectra taken in nitrobenzene after the sample was cooled to room temperature revealed the 14:15 ratio to be 87.4:12.6. Because of the interconversion of 14 and 15 at 165° and under conditions necessary for their g.l.p.c. separation analysis was obtained on the mixture obtained from preparative g.l.p.c. (SE 30).

Anal. Calcd. for C₁₈H₁₉N₃ ([M⁺] 381): C, 50.39; H, 4.99. Found (381): C, 50.47; H, 4.85.

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