spectrum consistent with the structure of isocaranone; MS VI, 81, 67, 41, 69, 109, 108, 82; VII, 81, 67, 41, 82, 152, 55, 95.

Compounds IX and X (RRT = 2.50 and 2.97) were identified as *trans*-2-caren-4-ol and *trans*-3(10)-caren-4-ol, respectively. An authentic sample of X was obtained by isomerization of 3-carene oxide over aluminum isopropoxide (AIP).[8]

Peak XIII (RRT = 2.13) was identified as *cis*-2,8,(9)-*p*-menthadien-1-ol by comparison of retention time and mass spectrum with those of an authentic sample prepared by isomerization of 2-carene oxide with metatitanic acid[13]: MS 134, 119, 91, 109, 79, 43, 41, 152 (M^+); reference 91, 119, 134, 41, 79, 77, 43, 152 (M^+).

Peaks XIV and XVI (RRT = 2.58 and 3.13) had nearly identical mass spectra. The base peak in the mass spectrum at *m/e* 59 (Me_2COH^+) suggested loss of the dimethylcarbinol ion. A fragment of *m/e* 94 ($C_7H_{10}^+$) together with the 59 fragment suggested structures of α- and β-phellandren-8-ol for the pair of isomers, XIV, and XVI, respectively. The IR and NMR spectra of the isolated compound XIV were consistent with those of an authentic sample [IR 3400, 1170, 1130 cm^{-1} tertiary alcohol; NMR δ 1.18 (s, 6, $>C(CH_3)_2$), 1.70 (s, 3, vinylic CH_3), 2.1–2.3 (m, 3, $>CH_2$ and $>CH$), 2.56 (s, 1, OH), 5.3–5.6 (broad, 1) and 5.79 ppm (d, 2) for vinylic protons]. The structure of XVI was only inferred because its mass spectrum was almost identical with that of compound XIV [MS XIV, 59, 79, 94, 91, 93, 119, 77, 134 ($M^+ - 18$); XVI, 59, 79, 94, 91, 43, 77, 119, 134 ($M^+ - 18$)].

GLC peaks II, III, VIII, XI, XII, XV, and XVII (RRT = 0.42, 0.55, 2.77, 0.46, 0.96, 3.03, and 4.13) were identified as 1,5,8(9)-*p*-menthatriene, *p*-cymene, carvenone, 1(7),2,8(9)-*p*-menthatriene, α,*p*-dimethylstyrene, a mixture of *cis*- and *trans*-1,8(9)-*p*-menthadien-3-ol and *p*-cymen-8-ol, respectively, by comparison of GLC retention times and mass spectra with reference materials.

References and Notes

(1) Epoxide Rearrangement 11. Part 10: see ref 16.
(2) I. C. Nigam and L. Levi, *Can. J. Chem.*, **46**, 1944 (1968).
(3) R. L. Settine, G. L. Parks, and G. L. K. Hunter, *J. Org. Chem.*, **29**, 616 (1964).
(4) E. E. Royals and L. L. Harrell, Jr., *J. Am. Chem. Soc.*, **77**, 3405 (1955).
(5) J. M. Coxon, E. Dansted, M. P. Hartshorn, and K. E. Richards, *Tetrahedron*, **25**, 3307 (1969).
(6) J. P. Montheard and Y. Chretien-Bessiere, *Bull. Soc. Chim. Fr.*, 336 (1968).
(7) M. P. Hartshorn, D. N. Kirk, and A. F. A. Wallis, *J. Chem. Soc.*, 5494 (1964).
(8) E. I. Eschinasi, *Isr. J. Chem.*, **6**, 713 (1968).
(9) R. L. Settine and C. McDaniel, *J. Org. Chem.*, **32**, 2910 (1967).
(10) Z. G. Isaeva and G. A. Bakaleinik, *Dokl. Akad. Nauk SSSR*, **176**, 1310 (1967); *Chem. Abstr.*, **68**, 95988*u* (1968).
(11) V. S. Joshi, N. P. Damodaran, and S. Dev, *Tetrahedron*, **24**, 5817 (1968); **27**, 459, 475 (1971).
(12) *Chem. Abstr.*, **76**, 14728*z* (1972).
(13) J. O. Bledsoe, Jr., J. M. Derfer, and W. E. Johnson, Jr., U.S. Patent, 3 814 733 (1974).
(14) K. Arata, S. Akutagawa, and K. Tanabe, *J. Catal.*, **41**, 173 (1976).
(15) K. Arata, H. Takahashi, and K. Tanabe, *Rocz. Chem.*, **50**, 2101 (1976).
(16) K. Arata, S. Akutagawa, and K. Tanabe, to be published.
(17) H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).
(18) K. Tanabe, "Solid Acids and Bases", Academic Press, New York, N.Y., 1970, p 58.
(19) However, the direct rearrangement of 3-carene oxide to carvenone is reported to occur in the presence of boron trifluoride etherate; see P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4926 (1966).
(20) K. Arata and K. Tanabe, to be published.
(21) T. Iizuka, H. Hattori, Y. Ohno, J. Soma, and K. Tanabe, *J. Catal.*, **22**, 130 (1971).
(22) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hill, New York, N.Y., 1968, p 128.
(23) This type opening of 2-carene oxide by acids was also reported by Ohloff and Giersch, *Helv. Chim. Acta*, **51**, 1328 (1968).
(24) E. J. Corey, H. J. Burke, and W. A. Remers, *J. Am. Chem. Soc.*, **78**, 180 (1956).
(25) J. R. B. Campbell, A. M. Islam, and R. A. Raphael, *J. Chem. Soc.*, 4096 (1956).
(26) J. A. Berson and M. R. Willeott, *J. Am. Chem. Soc.*, **88**, 2494 (1966).
(27) J. G. Grasselli, "Atlas of Spectral Data and Physical Constants for Organic Compounds", CRC Press, 1973.

Intramolecular 1,3-Dipolar Cycloaddition Reactions of Alkenyl-Substituted Nitrile Imines[1]

Albert Padwa,* Steven Nahm, and Eisuke Sato

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

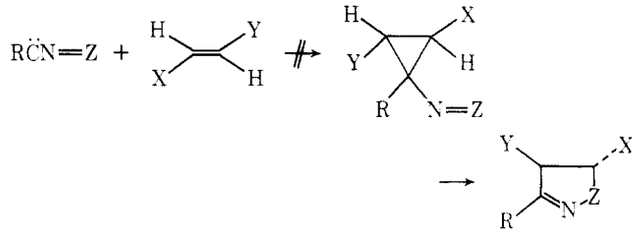
Received October 26, 1977

A series of nitrile imines bearing alkenyl substituents on the nitrogen atom of the 1,3 dipole were generated in situ by the photolysis of 2-alkenyl-5-phenyl-substituted tetrazoles or by the base treatment of 1-chlorohydrazones. Intramolecular 1,3-dipolar cycloaddition leading to substituted pyrazoles was the exclusive reaction observed. When the nitrile imine was generated in the presence of an active dipolarophile, bimolecular 1,3-dipolar cycloaddition occurred. Under these conditions, the intramolecular cycloaddition reaction is entirely suppressed. The mode of internal cycloaddition of the allyl-substituted nitrile imine is very different from that previously encountered in the closely related nitrile ylide system. With that system, intramolecular 1,1 cycloaddition was the predominant mode of reaction. Insight into the differences in chemical behavior of the two nitrilium betaines was obtained from molecular orbital calculations. These calculations show that the introduction of a nitrogen atom in the 1,3 dipole results in a significant flattening of the molecule. As the dipole becomes less bent it is less likely to undergo the 1,1-cycloaddition reaction.

The thermally induced addition of 1,3 dipoles to multiple bonds is an extremely versatile and important reaction.[2-4] Numerous possibilities for variation are available by changing the structure of both the dipolarophile and dipole. Some of the more interesting members of the 1,3-dipole family are the nitrilium betaines.[2] This class of 1,3 dipoles always contains nitrogen as the middle atom since only this element can supply an unshared electron pair while in the trivalent neutral state. Among the possible geometric forms of a nitrilium betaine, a carbene structure can be envisaged which makes conceivable a 1,1 cycloaddition of this 1,3 dipole. The possibility that

$$[\overset{-}{R}C{=}\overset{+}{N}{=}Z \leftrightarrow R\ddot{C}{-}\overset{+}{N}Z \leftrightarrow R\overset{+}{C}{=}N\overset{-}{Z} \leftrightarrow R\ddot{C}N{=}Z]$$
$$Z = C, N, O$$

the 1,3-dipolar cycloaddition reaction of a nitrilium betaine with a dipolarophile actually proceeds via a 1,1 cycloaddition followed by ring expansion has been discounted by Huisgen and co-workers.[5] These workers were able to show that three-membered rings are not primary products in the cy-



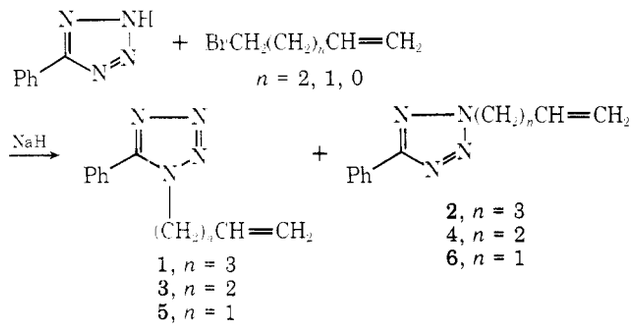
0022-3263/78/1943-1664$01.00/0

cloaddition reaction leading to five-membered heterocycles with nitrilium betaines.

Recent results from our laboratory have shown, however, that there are two pathways by which nitrile ylides can react with multiple π bonds.[6-9] The most frequently encountered path involves a "parallel-plane approach of addends" and can be considered to be an orbital symmetry-allowed [4 + 2] concerted process.[2] The other path, designated as 1,1 cycloaddition, operates only in certain intramolecular cases. It occurs when the p orbitals of the dipolarophile have been deliberately constrained to attack perpendicular to the nitrile ylide plane. Since our original report of this novel phenomenon appeared, a related intramolecular carbene type of 1,1 cycloaddition of a nitrilimine has been reported by Garanti and co-workers.[10] An analogous 1,1 cycloaddition of benzonitrile oxide has also been proposed to occur in the cycloaddition of benzonitrile oxide with several 4-arylideneisoxazol-5-ones.[11] As a further consequence of our interest in this area, we thought it worthwhile to determine whether additional examples of carbenoid activity of nitrilium betaines could be uncovered. In this paper we describe some of our efforts involving the generation and chemistry of a number of nitrilimines containing unsaturation several atoms away from the dipole center.

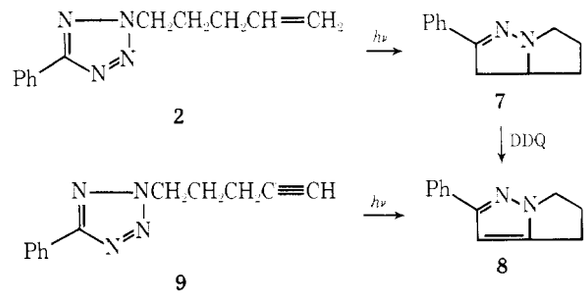
Results and Discussion

As our first model we chose to investigate the photochemistry of a series of 2-alkenyl-5-phenyl-substituted tetrazoles. The photolysis[12] and/or thermolysis[13] of 2,5-disubstituted tetrazoles represents a convenient method for the in situ generation of nitrilimines.[14] The same products are generally obtained from cycloaddition reactions with the products of tetrazole photolysis as from nitrilimines generated by the standard procedure of treating hydrazonyl chlorides with base.[15,16] The synthesis of these 2-alkenyl-5-phenyl-substituted tetrazoles was straightforward and involved the reaction of 5-phenyltetrazole with an appropriately substituted bromoalkene in the presence of base. Under these conditions a mixture of 1- and 2-alkenyl-substituted tetrazoles (ratio ca. 1:20) was obtained in good yield. Much work on the alkylation of tetrazoles has been carried out,[17-19] and in general it appears that electron-donating substituents at the 5 position favor alkylation at the N_1 position of tetrazole anions, while electron-withdrawing 5 substituents favor the 2 position.[20] The predominant formation of the 2-alkenyl-substituted tetrazoles (i.e., **2, 4,** and **6**) is perfectly consistent with the reported trends of tetrazole anion alkylation.[14]



The structural assignments were made on the basis of UV and NMR spectroscopy. Evidence has been obtained demonstrating that in a given pair of structural isomers the 2,5-disubstituted structure exhibits an absorption maximum at longer wavelengths than the 1,5-disubstituted isomer.[21] As expected, the UV spectra of tetrazoles **2, 4,** and **6** exhibited a maximum at 239 nm (ϵ ca. 17 000), while the maximum for the corresponding 1,5-disubstituted tetrazoles (i.e., **1, 3,** and **5**) was shifted to slightly shorter wavelength [232 nm (ϵ 9000)] and possessed a smaller extinction coefficient. Structural assignments were further strengthened by NMR measurements. Previous work in the literature has established that the phenyl protons of 5-phenyl-1-substituted tetrazoles appear as a singlet, while with the corresponding 2-substituted tetrazoles these protons appear as a multiplet with the ortho protons approximately 0.7 Hz downfield from the meta/para protons.[22] This was also the case with the above 1- and 2-alkenyl-substituted tetrazoles. The shielding of the meta/para protons with tetrazoles **2, 4,** and **6** can be attributed to an electron-donating resonance interaction between the two rings which is absent or greatly diminished owing to steric loss of coplanarity in the 1-alkenyl isomer. Similar effects have been observed for a series of related aryl azoles.[23]

With the structural assignments of these 2,5-disubstituted tetrazoles firmly established, a detailed study of their photochemical behavior was undertaken. Irradiation of 2-(4-pentenyl)-5-phenyltetrazole (**2**) in benzene using a 450-W Hanovia immersion apparatus equipped with a Corex filter sleeve led to the complete consumption of reactant in 60 min. The only product obtained was 3a,4,5,6-tetrahydro-2-phenyl-3*H*-pyrrolo[1,2-*b*]pyrazole (**7**): NMR ($CDCl_3$, 60 MHz)

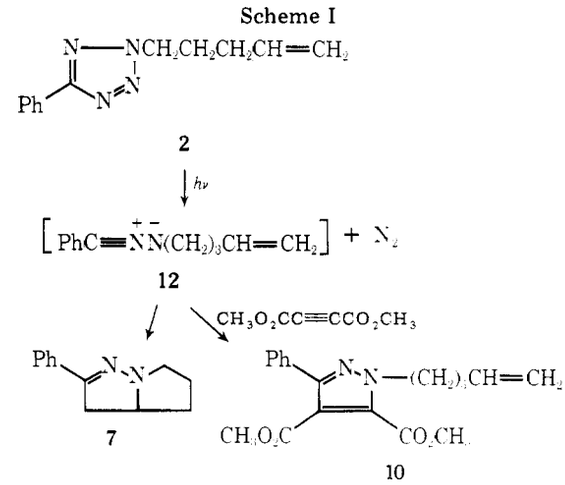


2 7 9 8

τ 8.04–8.90 (m, 4 H), 5.94–7.10 (m, 5 H), 2.70–2.87 (m, 3 H), 2.37–2.60 (m, 2 H). This structure was further supported by DDQ oxidation to 5,6-dihydro-2-phenyl-4*H*-pyrrolo[1,2-*b*]-pyrazole (**8**): NMR ($CDCl_3$, 60 MHz) τ 7.0–7.7 (m, 4 H), 5.87 (t, 2 H, J = 7.0 Hz), 3.75 (s, 1 H), 2.57–2.73 (m, 3 H), 2.17–2.37 (m, 2 H). Structure **8** was verified by an independent synthesis which involved the photolysis of 2-(4-pentynyl)-5-phenyltetrazole (**9**).

The formation of structure **7** (and/or **8**) could be completely suppressed when the irradiation of **2** (and/or **9**) was carried out in the presence of excess dimethyl acetylenedicarboxylate. The only product formed under these conditions was the expected 1,3-dipolar cycloadduct **10** (and/or **11**) (Scheme I). Similar results were obtained when methyl acrylate was used as the trapping reagent with tetrazole **9**. Clearly, nitrilimine **12** is an intermediate in these reactions, and **7** (or **8**) arises by

Scheme I

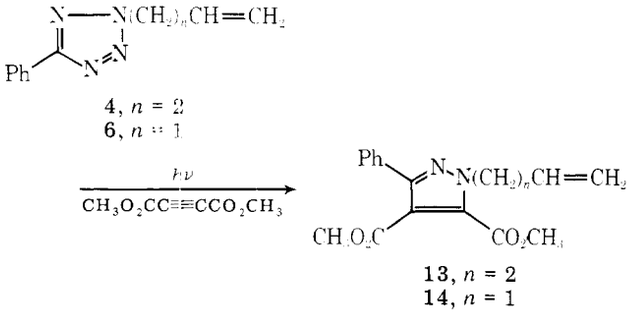


2 12 7 10

intramolecular 1,3-dipolar cycloaddition of the transient nitrilimine with the neighboring double bond (Scheme I).

A number of reports in the literature by Garanti and coworkers[24-26] have shown that nitrilimines undergo smooth intramolecular 1,3-dipolar cycloadditions.[27] In order for the intramolecular 1,3-dipolar cycloaddition reaction to proceed, two criteria must be met. First, the distance between the two reacting centers should be sufficiently short so that effective three-center overlap of the nitrilimine with the dipolarophile can occur. Secondly, the atoms of the dipole and dipolarophile should be arranged in such a way as to allow attainment of the "two-plane orientation approach."[2] These criteria are readily satisfied with the nitrilimine (i.e., **12**) generated from the irradiation of tetrazole **2**. The intramolecular cyclization reaction of nitrilimine **12** is also of interest in that it involves cycloaddition with an unactivated olefin, a substrate which is generally unreactive toward nitrilimines.[28] The facility with which the above cycloaddition proceeds suggests that an extremely favorable entropy term, relative to the intermolecular reaction, offsets the unfavorable electronic factor.

Whereas tetrazole **2** was smoothly converted to pyrazole **7** on irradiation, photolysis of the homologous tetrazoles **4** and **6** resulted in the formation of polymeric material. When the irradiation of these compounds was carried out in the presence of dimethyl acetylenedicarboxylate, however, the expected 1,3-dipolar cycloadducts **13** and **14** were obtained in good

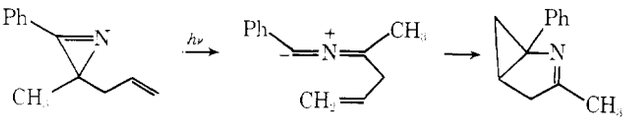


4, $n = 2$
6, $n = 1$

13, $n = 2$
14, $n = 1$

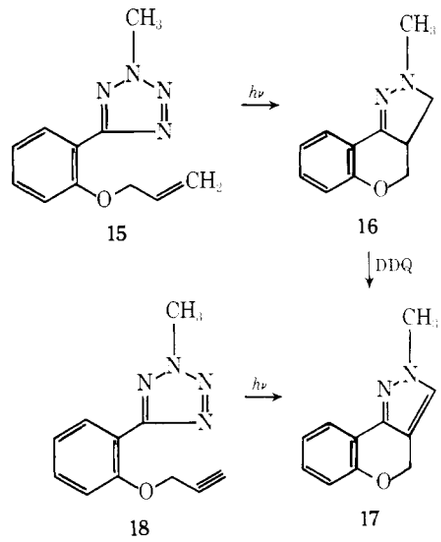
yield. All attempts to detect an intramolecular cycloadduct (1,3 or 1,1) from the nitrilimines derived from these tetrazoles failed. The isolation of cycloadducts **13** and **14** indicates that the expected nitrilimines are formed but that intramolecular cycloaddition does not occur. With the nitrilimines derived from tetrazole **4** or **6**, the methylene chain is not of sufficient length to allow the dipole and dipolarophile to approach each other in parallel planes. Consequently, intramolecular 1,3-dipolar cycloaddition does not occur. The situation here is very different from that observed with the 2-(4-pentenyl)tetrazole **2**. With tetrazole **2**, the transition state for cycloaddition allows easy attainment of the "parallel-plane approach," and consequently intramolecular 1,3-dipolar cycloaddition of the initially generated nitrilimine readily occurs.

While this analysis satisfactorily explains the absence of an intramolecular 1,3-dipolar cycloaddition with tetrazole **6**, it does not account for the absence of a 1,1 cycloadduct with the 2-allyl-substituted tetrazole.[29] Allyl-substituted nitrile ylides are known to undergo smooth 1,1 cycloaddition to give azabicyclo[3.1.0]hex-2-enes.[6-8] The situation with the nitrilimine



class of 1,3 dipoles is clearly very different from that previously encountered with the closely related nitrile ylide system. The nature of the Z atom of the nitrilium betaine seems to play an important role in controlling the intramolecular 1,1-cycloaddition reaction.

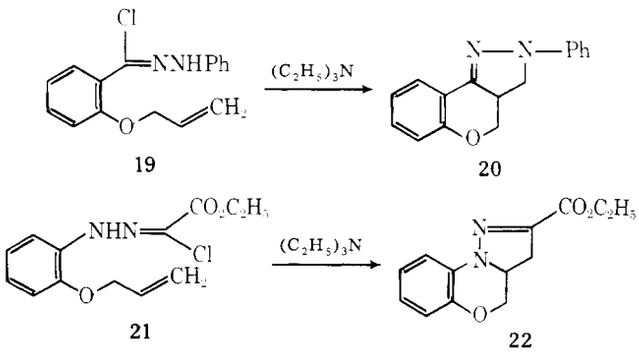
This contention was further supported by a study of the photolysis of 2-methyl-5-(*o*-allyloxyphenyl)tetrazole (**15**). Irradiation of tetrazole **15** in benzene afforded 2,3,3a,4-tetrahydro-2-methyl[*l*]benzopyrano[4,3-*c*]pyrazole (**16**) as the exclusive cycloadduct in 88% yield: NMR ($CDCl_3$, 60 MHz) τ 7.37–7.80 (m, 1 H), 7.12 (s, 3 H), 6.0–6.75 (m, 3 H), 5.27–5.57 (m, 1 H), 2.64–3.30 (m, 3 H), 2.20–2.44 (m, 1 H). The DDQ oxidation of **16** led to the corresponding dihydrobenzopyrano[4,3-*b*]pyrazole **17**, thus providing chemical support to the assigned structure. Compound **17** could also be independently prepared from the irradiation of (*o*-propargyloxyphenyl)tetrazole **18**.



15 **16** **18** **17**

It should be noted that *o*-allyloxyphenyl-substituted nitrile ylides have previously been found to undergo both 1,1- and 1,3-cycloaddition reactions.[8] However, all attempts to detect a 1,1 cycloadduct from the irradiation of tetrazole **15** failed. The exclusive formation of a 1,3-dipolar cycloadduct from the nitrilimine derived from tetrazole **15** provides further evidence that the type of reaction entered into by these nitrilium betaines is strongly dependent on the nature of the Z atom of the 1,3 dipole.

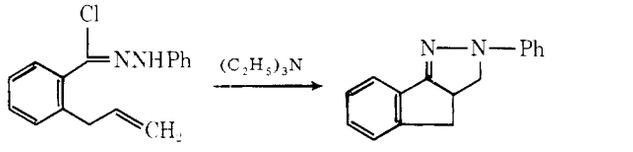
Recent results in the literature have shown that significant differences in the reactivity of a 1,3 dipole can occur when it is generated in the ground state or in an excited state.[30] In order to determine whether the mode of intramolecular cycloaddition of these nitrilimines is related to the manner in which they are generated, we decided to investigate the base-induced chemistry of hydrazonyl chlorides **19** and **21**. Reaction of triethylamine with a benzene solution of **19** at 80 °C produces triethylammonium chloride and 2,3,3a,4-tetrahydro-2-phenyl[*l*]benzopyrano[4,3-*c*]pyrazole (**20**): mp 99–100 °C; NMR ($CDCl_3$, 60 MHz) τ 5.76–7.02 (m, 4 H), 5.40 (dd, 1 H, J = 10.0, 5.0 Hz), 2.6–3.3 (m, 8 H), 2.20 (m, 1 H)). A similar reaction of hydrazonyl chloride **21** with triethylamine afforded a 82% yield of 2-carboethoxy-3,3a-dihydro-4*H*-pyrazolo[5,1-*c*][1,4]benzoxazine (**22**) as the only detectable cycloadduct.[31]



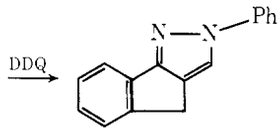
19 **20** **21** **22**

The close similarity in the behavior of all of these nitrilimines strongly suggests that the mode of internal cycloaddition is independent of the precursor used to generate the dipole.

We also studied the intramolecular dipolar cycloaddition reaction of the nitrilimine generated from the base treatment of 1-(*o*-allylphenyl)-*N*-(phenylhydrazidoyl) chloride (**23**). The

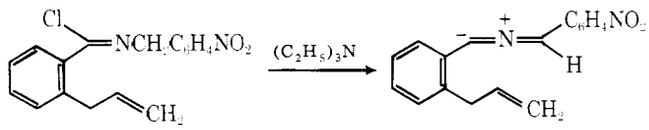


23 **24**

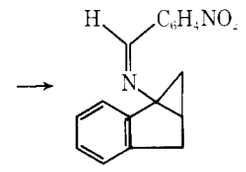


25

only product obtained in this reaction was 2,3,3a,4-tetrahydro-2-phenylindeno[1,2-*c*]pyrazole (**24**). This product was identified on the basis of its characteristic 270-MHz NMR spectrum ($CDCl_3$) which showed a set of doublet of doublets at τ 7.29 (1 H, J = 15.4, 7.3 Hz), 6.92 (1 H, J = 14.3, 9.6 Hz), and 6.74 (1 H, J = 15.4, 8.8 Hz), a multiplet centered at τ 6.39 (1 H), triplets at τ 5.71 (1 H, J = 9.6 Hz) and 3.24 (1 H, J = 6.0 Hz), and a multiplet for the aromatic protons at τ 2.30–3.00 (8 H). This structure was supported by its ready oxidation with DDQ to pyrazole **25.** The intramolecular cyclization of **23** is a particularly interesting case in that it proceeds exclusively in the 1,3 sense. The closely related nitrile ylide **27,**



26 **27**



28

generated from the base treatment of imidoyl chloride **26,** had previously been found to undergo exclusive 1,1 cycloaddition.[7]

A major aspect of interest requiring discussion involves the substantially different chemical behavior exhibited by these unsaturated nitrilium betaines toward intramolecular dipolar cycloaddition. In the present investigation, nitrilimines containing unsaturation four bonds away from the dipole center undergo cycloaddition exclusively in the 1,3 sense. The structurally related nitrile ylide systems, on the other hand, undergo both 1,1 and 1,3 cycloaddition. Since the geometry of approach of the dipole and dipolarophile centers with both systems is very similar, steric factors can not account for the divergent behavior observed. Insight into the difference in chemical behavior of the two nitrilium betaines can be gleaned from molecular orbital calculations. Recent ab initio LCAO–MO–SCF calculations by Houk and co-workers[32,33] have shown that nitrile ylides exist preferentially in the bent form with an HCN angle of 114–116°. These findings indicate that the most stable form of a nitrile ylide resembles a bent allenyl anion rather than a linear propargyl anion. The HOMO and second LUMO of the bent ylide bear a strong resemblance to the HOMO and LUMO of a singlet carbene. Carbenes are known to react readily with double bonds,[34] thereby providing good precedent for the formation of the 1,1 cycloadduct. This type of reaction will only occur when the alkene has been deliberately constrained to attack perpendicular to the CNC plane of the bent nitrile ylide.

Houk's group has also carried out optimizations on the geometry of the parent nitrilimine ($HC{\equiv}N^+NH^-$) and has found that the dipole is quite flexible. The STO-3G minimum suggests bent geometry with the bent form being favored by 2.2 kcal/mol over the linear form.[32] However, at the 4–31G level, the linear species was favored over the bent form by 3.9 kcal/mol.[32,33] In contrast, the bent nitrile ylide has been calculated to be 11.1 kcal/mol (4–31G) more stable than the linear form. Thus, replacement of the C_3 carbon atom of the nitrile ylide with a nitrogen atom results in a significant straightening of the molecule. More recent calculations show that the introduction of a phenyl group at C_1 further straightens the dipole.[35] Clearly, the geometric features of the nitrile ylide and nitrilimine are significantly different. The increasing stability of the linear geometry relative to the bent form, as the electronegativity of the Z terminus increases ($RC{\equiv}N^+Z^-$), can be attributed to the fact that the linear structure places more negative charge on the Z atom and possesses less N–Z double-bond character. The valence bond structure, $RC{\equiv}N^+NR^-$, is a good representation of the electronic structure of the nitrilimine, whereas the ylide can best be described by the $R\ddot{C}N{=}CR_2$ (carbene-like) designation. As the dipole becomes less bent it is less likely to undergo the 1,1-cycloaddition reaction. We believe that this explanation satisfactorily accounts for the propensity of these unsaturated nitrilimines to undergo intramolecular dipolar cycloaddition in the 1,3 sense.

We are continuing to explore the scope and mechanistic details of intramolecular nitrilimine cycloadditions and look forward to determining whether it will be possible to induce 1,1 cycloadditions of this dipole with related systems.

Experimental Section[36]

Preparation of 2-(4-Pentenyl)-5-phenyltetrazole (2). A 1.46-g sample of 5-phenyltetrazole[37] in 10 mL of dimethylformamide was added dropwise to an ice-cooled suspension containing 480 mg of sodium hydride in 3 mL of dimethylformamide. After the evolution of gas had ceased, 1.49 g of 5-bromo-1-pentene in 5 mL of dimethylformamide was added and the mixture was allowed to stir at 25 °C for 12 h. At the end of this time the mixture was poured onto 50 mL of ice water and extracted with benzene. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The resulting yellow oil was subjected to dry column chromatography using methylene chloride as the eluent. The first component eluted from the column contained 1.40 g (65%) of a colorless oil, bp 180–181 °C (0.1 mm), whose structure was assigned as 2-(4-pentenyl)-5-phenyltetrazole (**2**): IR (neat) 6.05, 6.55, 6.80, 6.90, 7.35, 8.32, 9.25, 9.50, 9.70, 10.85, 12.60, 13.65, 14.40 μm; UV (95% ethanol) 239 nm (ϵ 17 100); NMR ($CDCl_3$, 60 MHz) τ 7.73–7.93 (m, 4 H), 4.8–5.5 (m, 4 H), 4.0–4.6 (m, 1 H), 2.4–2.65 (m, 3 H), 1.80–2.0 (m, 2 H); MS *m/e* 214 (M^+), 186, 185, 158, 131, 129, 115, 77.

Anal. Calcd for $C_{12}H_{14}N_4$: C, 67.26; H, 6.59; N, 26.15. Found: C, 67.21; H, 6.66; N, 26.04.

The second component eluted from the column contained 70 mg (3%) of 1-(4-pentenyl)-5-phenyltetrazole (**1**) as a colorless oil: bp 165 °C (0.05 mm); IR (neat) 6.10, 6.55, 6.85, 7.15, 8.98, 9.25, 10.05, 10.85, 12.80, 13.60, 14.35 μm; UV (95% ethanol) 231 nm (ϵ 8950); NMR ($CDCl_3$, 60 MHz) τ 7.8–8.0 (m, 4 H), 4.8–5.65 (m, 4 H), 4.0–4.7 (m, 1 H), 2.37 (s, 5 H); MS *m/e* 214 (M^+), 118, 104, 83, 77, 68 (base).

Anal. Calcd for $C_{12}H_{14}N_4$: C, 67.26; H, 6.59; N, 26.15. Found: C, 67.43; H, 6.54; N, 26.32.

Irradiation of 2-(4-Pentenyl)-5-phenyltetrazole (2). A solution containing 214 mg of tetrazole **2** in 100 mL of benzene was irradiated through a Corex filter sleeve for 1 h. Removal of the solvent under reduced pressure left a pale yellow oil which was purified by thick-layer chromatography using a 3:1 methylene chloride/ethyl acetate mixture as the eluent. The major component (83 mg, 45%) was a clear oil, bp 135 °C (0.08 mm), and was identified as 3a,4,5,6-tetrahydro-2-phenyl-3*H*-pyrrolo[1,2-*b*]pyrazole (**7**) on the basis of the following

data: IR (neat) 6.28, 6.68, 6.90, 7.40, 8.45, 8.96, 9.15, 9.54, 10.25, 10.88, 13.10, 14.40 μm; UV (95% ethanol) 285 nm (ε 7600), 219 (6300); NMR ($CDCl_3$, 60 MHz) τ 8.04–8.90 (m, 4 H), 5.94–7.10 (m, 5 H), 2.70–2.87 (m, 3 H), 2.37–2.60 (m, 2 H); MS *m/e* 186 (M^+), 185, 131, 77.

Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.05. Found: C, 77.05; H, 7.71; N, 14.78.

The nitrilimine derived from the photolysis of tetrazole **2** could be trapped with dimethyl acetylenedicarboxylate. A solution containing 212 mg of tetrazole **2** and 1.42 g of dimethyl acetylenedicarboxylate in 120 mL of benzene was irradiated through a Corex filter sleeve for 8 h. The solvent was removed under reduced pressure, and the residual oil was purified by thick-layer chromatography using methylene chloride as the eluent. The major component isolated was a yellow oil which was distilled at 165 °C (0.04 mm) to give 1-(4-pentenyl)-3-phenyl-4,5-dicarbomethoxypyrazole (**10**) in 77% yield: IR (neat) 5.79, 6.58, 6.91, 8.00, 8.65, 9.10, 9.45, 10.80, 12.10, 12.55, 12.90, 14.30 μm; NMR ($CDCl_3$, 60 MHz) τ 7.86–8.20 (m, 4 H), 6.22 (s, 3 H), 6.13 (s, 3 H), 5.44–5.77 (m, 2 H), 4.84–5.20 (m, 2 H), 3.94–4.57 (m, 1 H), 2.30–2.84 (m, 5 H); UV (95% ethanol) 232 nm (ε 21 200); MS *m/e* 328 (M^+), 327 (base), 274, 273, 269, 129, 113, 77.

Preparation of 2-(4-Pentynyl)-5-phenyltetrazole (9). A 1.46-g sample of 5-phenyltetrazole in 10 mL of dimethylformamide was added dropwise to an ice-cooled suspension containing 480 mg of sodium hydride in 3 mL of dimethylformamide. After the evolution of gas had ceased, 1.03 g of 5-chloro-1-pentyne in 5 mL of dimethylformamide was added and the mixture was stirred at 80 °C for 3 h. At the end of this time the mixture was poured onto 50 mL of ice water and extracted with benzene. The benzene extracts were dried over magnesium sulfate and concentrated under reduced pressure. The resulting yellow oil was subjected to dry column chromatography using methylene chloride as the eluent. The first component eluted from the column contained 1.2 g (57%) of a colorless oil, bp 190 °C (0.5 mm), whose structure was assigned as 2-(4-pentynyl)-5-phenyltetrazole (**9**): IR (neat) 4.65, 6.50, 6.75, 6.85, 7.15 μm; UV (95% ethanol) 239 nm (ε 16 500); NMR ($CDCl_3$, 60 MHz) τ 7.50–7.98 (m, 5 H), 5.0–5.36 (m, 2 H), 2.50–2.64 (m, 3 H), 1.84–2.00 (m, 2 H); MS *m/e* 212 (M^+), 184, 183, 131, 128, 104 (base), 77.

Anal. Calcd for $C_{12}H_{12}N_4$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.68; H, 5.72; N, 26.53.

The second component isolated from the column contained 62 mg (3%) of 1-(4-pentynyl)-5-phenyltetrazole: IR (KBr) 4.50, 6.80, 6.95, 7.05, 7.20 μm; NMR ($CDCl_3$) τ 7.74–8.10 (m, 5 H), 5.18–5.42 (m, 2 H), 2.47 (broad s, 5 H); MS *m/e* 212 (M^+), 191, 189, 117, 105, 104, 103, 91, 78, 75 (base); UV (95% ethanol) 232 nm (ε 9000).

Anal. Calcd for $C_{12}H_{12}N_4$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.84; H, 5.82; N, 26.28.

Irradiation of 2-(4-Pentynyl)-5-phenyltetrazole (9). A solution containing 212 mg of tetrazole **9** in 120 mL of benzene was irradiated with a 450-W medium-pressure lamp through a Corex filter sleeve for 2.5 h. Removal of the solvent under reduced pressure left a yellow oil which was purified by thick-layer chromatography using methylene chloride as the eluent. The major component isolated (90 mg, 49%) was a colorless solid, mp 80–81 °C, whose structure was assigned as 5,6-dihydro-2-phenyl-4*H*-pyrrolo[1,2-*b*]pyrazole (**8**) on the basis of the following data: IR (KBr) 6.20, 6.45, 6.60, 6.85, 7.00, 7.20, 7.50, 7.60, 9.18, 9.60, 10.25, 12.45, 13.05, 14.55 μm; UV (95% ethanol) 254 nm (ε 18 200); NMR ($CDCl_3$, 60 MHz) τ 7.0–7.7 (m, 4 H), 5.87 (t, 2 H, J = 7.0 Hz), 3.75 (s, 1 H), 2.57–2.73 (m, 3 H), 2.17–2.37 (m, 2 H); MS *m/e* 184 (M^+ and base), 156, 124, 102, 95, 77.

Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 78.21; H, 6.50; N, 14.99.

The structure of this material was verified by the DDQ oxidation of pyrazole **7**. A mixture of 80 mg of **7** and 100 mg of DDQ in 5 mL of benzene was allowed to reflux for 24 h. Removal of the solvent under reduced pressure left a dark red residue which was subjected to thick-layer chromatography to give **8** in 85% yield. The spectroscopic properties of **8** prepared from the oxidation of **7** were identical with those obtained from the iradiation of tetrazole **9**.

The initially produced nitrilimine could be trapped by carrying out the irradiation of **9** in the presence of methyl acrylate or dimethyl acetylenedicarboxylate. A solution containing 212 mg of tetrazole **9** and 861 mg of methyl acrylate in 120 mL of benzene was irradiated through a Corex filter sleeve for 6 h. The solvent was then removed under reduced pressure, and the residual oil was purified by thick-layer chromatography using a 10:1 pentane/ethyl acetate mixture as the eluent. The major component was a colorless oil (190 mg, 68%), bp 180 °C (0.04 mm), whose structure was assigned as 1-(4-pentynyl)-3-phenyl-5-carbomethoxypyrazole on the basis of its spectral data: IR (KBr) 5.80, 6.50, 6.65, 6.80, 7.15, 7.95, 9.05, 10.40, 12.10, 13.05, 14.40 μm; UV (95% ethanol) 234 nm (ε 25 700); NMR ($CDCl_3$, 60 MHz) τ 7.80–8.16 (m, 5 H), 6.16 (s, 3 H), 5.25–5.46 (m, 2 H), 2.95 (s, 1 H), 2.45–2.85 (m, 3 H), 2.08–2.30 (m, 2 H); MS *m/e* 268 (M^+), 267 (base), 215, 183, 104.

Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.76; H, 6.10; N, 10.41.

A similar trapping experiment with dimethyl acetylenedicarboxylate gave a 58% yield of 1-(4-pentynyl)-3-phenyl-4,5-dicarbomethoxypyrazole (**11**) as a crystalline solid: mp 82–83 °C; IR (KBr) 5.73, 6.55, 6.90, 7.25, 8.00, 8.70, 9.05, 12.15, 13.70, 14.15 μm; UV (95% ethanol) 232 nm (ε 22 700); NMR ($CDCl_3$, 60 MHz) τ 7.70–8.04 (m, 5 H), 6.18 (s, 3 H), 6.08 (s, 3 H), 5.46 (t, 2 H, J = 7.0 Hz), 2.20–2.70 (m, 5 H); MS *m/e* 326 (M^+), 325 (base), 273, 77.

Anal. Calcd for $C_{18}H_{18}N_2O_4$: C, 66.24; H, 5.56; N, 8.58. Found: C, 66.00; H, 5.52; N, 8.50.

Preparation and Irradiation of 2-(3-Butenyl)-5-phenyltetrazole (4). A 1.46-g sample of 5-phenyltetrazole in 10 mL of dimethylformamide was added dropwise to an ice-cooled suspension containing 480 mg of sodium hydride in 3 mL of dimethylformamide. After the evolution of gas had ceased, 1.35 g of 4-bromo-1-butene in 5 mL of dimethylformamide was added and the mixture was stirred at 25 °C for 12 h. At the end of this time the mixture was poured onto 50 mL of ice water and extracted with benzene. The benzene extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure to give an orange residue. The residue was subjected to dry column chromatography using methylene chloride as the eluent. The first component isolated from the column contained 1.17 g (59%) of a colorless oil, bp 165 °C (0.15 mm), whose structure was assigned as 2-(3-butenyl)-5-phenyltetrazole (**4**) on the basis of the following data: IR (neat) 6.05, 6.55, 6.85, 6.95, 7.30, 9.25, 9.50, 9.65, 9.95, 10.70, 12.60, 13.60, 14.40 μm; UV (95% ethanol) 238 nm (ε 15 900); NMR ($CDCl_3$, 60 MHz) τ 7.20 (g, 2 H, J = 7.0 Hz), 5.33 (t, 2 H, J = 7.0 Hz), 4.70–5.10 (m, 2 H), 3.67–4.50 (m, 1 H), 2.43–2.63 (m, 3 H), 1.80–1.97 (m, 2 H); MS *m/e* 200 (M^+), 131, 104 (base), 77.

Anal. Calcd for $C_{11}H_{12}N_4$: C, 65.98; H, 6.04; N, 27.98. Found: C, 65.99; H, 6.37; N, 28.11.

The second component isolated from the column contained 74 mg (4%) of 1-(3-butenyl)-5-phenyltetrazole (**3**) as a colorless oil: bp 180 °C (0.2 mm); IR (neat) 6.05, 6.50, 6.80, 7.10, 8.95, 10.05, 10.70, 12.75, 13.60, 14.40 μm; UV (95% ethanol) 231 nm (ε 10 400); NMR ($CDCl_3$, 60 MHz) τ 7.33 (q, 2 H, J = 7.0 Hz), 5.50 (t, 2 H, J = 7.0 Hz), 4.87–5.20 (m, 2 H), 3.97–4.60 (m, 1 H), 2.40 (s, 5 H); MS *m/e* 200 (M^+), 185, 144, 131, 119, 105, 78 (base).

Anal. Calcd for $C_{11}H_{12}N_4$: C, 65.98; H, 6.04; N, 27.98. Found: C, 66.12; H, 5.98; N, 28.26.

A solution containing 200 mg of tetrazole **4** and 1.42 g of dimethyl acetylenedicarboxylate in 120 mL of benzene was irradiated through a Corex filter sleeve for 4 h. Removal of the solvent left a yellow oil which was subjected to dry column chromatography (alumina) using chloroform as the eluent. The major component isolated contained 220 mg (70%) of a colorless oil, whose structure was assigned as 1-(3-butenyl)-3-phenyl-4,5-dicarbomethoxypyrazole (**13**) on the basis of the following data: IR (neat) 5.75, 6.05, 6.52, 6.90, 7.90, 8.65, 9.20, 9.50, 9.70, 10.75, 12.10, 12.60, 12.85, 14.30 μm; UV (95% ethanol) 234 nm (ε 22 100); NMR ($CDCl_3$, 60 MHz) τ 7.36 (q, 2 H, J = 7.0 Hz), 6.22 (s, 3 H), 6.12 (s, 3 H), 5.48 (t, 2 H, J = 7.0 Hz), 4.74–5.17 (m, 2 H), 3.64–4.54 (m, 1 H), 2.24–2.80 (m, 5 H); MS *m/e* 314 (M^+), 313, 273, 132, 131 (base), 104, 77.

Anal. Calcd for $C_{17}H_{18}N_2O_4$: C, 64.95; H, 5.77; N, 8.91. Found: C, 65.26; H, 5.95; N, 9.20.

Preparation and Irradiation of 2-Allyl-5-phenyltetrazole (6). To a solution containing 2.9 g of 5-phenyltetrazole in 100 mL of 95% ethanol was added 5.1 g of silver nitrate in 10 mL of water. After stirring for 20 min, a 14% aqueous ammonia solution was added and 5.2 g of a gray solid was collected by filtration. A 2.5-g sample of the above silver salt was suspended in 20 mL of chloroform, and 6.0 g of allyl bromide was added. The mixture was heated at reflux for 24 h, and the solid precipitate was filtered off. The filtrate was concentrated under reduced pressure, and the resulting oil was subjected to dry column chromatography using methylene chloride as the eluent. The initial component isolated from the column contained 1.3 g (70%) of a colorless liquid, bp 178 °C (0.14 mm), whose structure was assigned as 2-allyl-5-phenyltetrazole (**6**): IR (neat) 6.03, 6.50, 6.78, 6.90, 8.35, 9.30, 9.55, 9.70, 10.05, 10.70, 12.60, 13.55, 14.40 μm; UV (95% ethanol) 239 nm (ε 16 700); NMR ($CDCl_3$, 60 MHz) τ 3.50–3.90 (m, 4 H), 3.60–4.24 (m, 1 H), 2.50–2.70 (m, 3 H), 1.80–2.00 (m, 2 H); MS *m/e* 130, 129 (base), 128, 115, 77.

Anal. Calcd for $C_{10}H_{10}N_4$: C, 64.50; H, 5.41; N, 30.09. Found: C, 64.74; H, 5.55; N, 29.94.

The second component isolated from the column contained 180 mg (10%) of 1-allyl-5-phenyltetrazole (**5**): IR (neat) 6.08, 6.20, 6.50, 6.80,

7.15, 7.60, 8.0, 8.95, 9.25, 10.05, 10.75, 12.70, 13.60, 14.35 μm; UV (95% ethanol) 231 nm (ε 10 500); NMR ($CDCl_3$, 60 MHz) τ 4.63–5.07 (m, 4 H), 3.57–4.23 (m, 1 H), 2.43 (m, 5 H); MS *m/e* 186 (M^+), 129 (base), 128, 115, 104, 103, 77.

Anal. Calcd for $C_{10}H_{10}N_4$: C, 64.50; H, 5.41; N, 30.09. Found: C, 64.76; H, 5.40; N, 29.86.

A solution containing 186 mg of tetrazole **6** and 1.42 g of dimethyl acetylenedicarboxylate in 120 mL of benzene was irradiated through a Corex filter for 6 h. Removal of the solvent left a yellow oil which was purified by alumina chromatography using chloroform as the eluent. The major component isolated (195 mg, 66%) was a colorless oil whose structure was assigned as 1-allyl-3-phenyl-4,5-dicarbomethoxypyrazole (**14**) on the basis of the following data: bp 165 °C (0.03 mm); IR (neat) 5.73, 6.50, 6.85, 7.90, 8.65, 9.20, 9.55, 9.70, 12.10, 12.60, 12.90, 14.30 μm; UV (95% ethanol) 236 nm (ε 18 000); NMR ($CDCl_3$, 60 MHz) τ 6.20 (s, 3 H), 6.12 (s, 3 H), 4.67–5.03 (m, 4 H), 3.64–4.30 (m, 1 H), 2.24–2.84 (m, 5 H); MS *m/e* 300 (M^+), 270, 269, 268, 239, 182, 163 (base).

Anal. Calcd for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33. Found: C, 64.19; H, 5.60; N, 9.48.

Preparation of 2-Methyl-5-(*o*-allyloxyphenyl)tetrazole (15). A mixture containing 10.1 g of 2-cyanophenol, 17.2 g of sodium azide, and 6.0 g of ammonium chloride in 50 mL of dimethylformamide was heated at reflux for 20 h. At the end of this time the reaction mixture was poured onto 300 mL of ice water and acidified with a 10% hydrochloric acid solution. The solid which formed was filtered off and recrystallized from ethanol/water to give 10.8 g (78%) of 5-(*o*-hydroxyphenyl)tetrazole, mp 224–225 °C.

A 1.62-g sample of the above tetrazole in 20 mL of dimethylformamide was added to an ice-cooled mixture containing 480 mg of sodium hydride in 3 mL of dimethylformamide. After the evolution of gas had ceased, 1.42 g of methyl iodide in 5 mL of dimethylformamide was added at 0 °C. The mixture was allowed to stir at 25 °C for 12 h and was then poured onto 50 mL of ice water. The solution was extracted with benzene, and the extracts were dried over magnesium sulfate and concentrated under reduced pressure. The resulting liquid was purified by dry column chromatography followed by distillation at 150 °C (0.1 mm) to give 756 mg (43%) of 2-methyl-5-(*o*-hydroxyphenyl)tetrazole as a crystalline solid: mp 59–60 °C; IR (neat) 3.05, 6.15, 6.30, 6.55, 6.83, 7.25, 8.05, 9.45, 9.60, 9.85, 11.90, 13.20, 13.80 μm; UV (95% ethanol) 295 nm (ε 5400), 241 (11 800); NMR ($CDCl_3$, 60 MHz) τ 5.58 (s, 3 H), 2.47–3.20 (m, 3 H), 1.99 (dd, 1 H, *J* = 7.0, 2.0 Hz), 0.38 (1 H, s); MS *m/e* 176 (M^+), 148, 119, 105, 77.

Anal. Calcd for $C_8H_8N_4O$: C, 54.54; H, 4.58; N, 31.80. Found: C, 54.74; H, 4.60; N, 32.13.

To a solution containing 706 mg of the above tetrazole in 10 mL of 95% ethanol was added 160 mg of sodium hydroxide in 5 mL of water followed by 605 mg of allyl bromide. The mixture was heated at 70 °C for 20 h and then poured onto 50 mL of ice water. The solution was extracted with benzene, and the benzene extracts were washed with a 10% sodium hydroxide solution and water and then dried over magnesium sulfate. Removal of the solvent left 662 mg (77%) of a colorless solid, mp 39–40 °C, whose structure was assigned as 2-methyl-5-(*o*-allyloxyphenyl)tetrazole (**15**): IR (KBr) 6.15, 6.25, 6.50, 6.70, 7.18, 7.79, 8.95, 9.50, 10.05, 10.70, 13.20, 13.80 μm; UV (95% ethanol) 288 nm (ε 4500), 235 (9900); NMR ($CDCl_3$, 60 MHz) τ 5.66 (s, 3 H), 5.27–5.47 (m, 2 H), 4.30–4.94 (m, 2 H), 3.60–4.24 (m, 1 H), 2.47–3.14 (m, 3 H), 2.05 (dd, 1 H, *J* = 7.0, 2.0 Hz); MS *m/e* 216 (M^+), 189, 188 (base), 145, 117, 115, 91, 77.

Anal. Calcd for $C_{11}H_{12}N_4O$: C, 61.09; H, 5.59; N, 25.91. Found: C, 61.26; H, 5.68; N, 26.04.

Irradiation of 2-Methyl-5-(*o*-allyloxyphenyl)tetrazole (15). A 216-mg sample of tetrazole **15** in 100 mL of benzene was irradiated through a Corex filter sleeve for 2 h. Removal of the solvent under reduced pressure left a yellow oil which was purified by thick-layer chromatography using a 5:2 methylene chloride/ethyl acetate mixture as the eluent. The major component contained 164 mg (88%) of a crystalline solid, mp 52–53 °C, whose structure was assigned as 2,3,3a,4-tetrahydro-2-methyl[*l*]benzopyrano[4,3-*c*]pyrazole (**16**) on the basis of the following data: IR (KBr) 6.22, 6.80, 6.90, 7.25, 7.65, 8.10, 8.25, 8.90, 9.05, 9.60, 9.90, 10.60, 11.95, 13.20 μm; UV (95% ethanol) 325 nm (ε 9950), 297 (6900); NMR ($CDCl_3$, 60 MHz) τ 7.37–7.80 (m, 1 H), 7.12 (s, 3 H), 6.0–6.75 (m, 3 H), 5.27–5.57 (m, 1 H), 2.64–3.30 (m, 3 H), 2.20–2.44 (m, 1 H); MS *m/e* 188 (M^+), 187 (base), 149, 115, 91.

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.88. Found: C, 69.86; H, 6.18; N, 14.58.

Preparation of 2-Methyl-5-(*o*-propargyloxyphenyl)tetrazole (18). To a solution containing 560 mg of 2-methyl-5-(*o*-hydroxyphenyl)tetrazole in 10 mL of 95% ethanol was added 130 mg of sodium hydroxide in 5 mL of water followed by 454 mg of propargyl bromide. The mixture was heated at 70 °C for 20 h and then poured onto 50 mL of ice water. The solution was extracted with benzene, and the benzene extracts were washed with a 10% sodium hydroxide solution and water and then dried over magnesium sulfate. Removal of the solvent left a yellow oil which was purified by dry column chromatography to give 350 mg (51%) of 2-methyl-5-(*o*-propargyloxyphenyl)tetrazole (**18**) as a crystalline solid: mp 81–82 °C; IR (KBr) 4.78, 6.22, 6.32, 6.60, 6.78, 7.24, 7.90, 8.18, 9.04, 9.51, 9.65, 9.75, 10.80, 13.40, 13.75 μm; UV (95% ethanol) 287 nm (ε 3900), 236 (11 300); NMR ($CDCl_3$, 60 MHz) τ 7.50 (t, 2 H, *J* = 2.0 Hz), 5.62 (s, 3 H), 5.20 (d, 2 H, *J* = 2.0 Hz), 2.4–2.97 (m, 3 H), 1.94–2.17 (dd, 1 H, *J* = 7.0, 2.0 Hz); MS *m/e* 214 (M^+), 186 (base), 185, 115, 77.

Anal. Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 26.16. Found: C, 61.84; H, 4.76; N, 26.34.

Irradiation of 2-Methyl-5-(*o*-propargyloxyphenyl)tetrazole (18). A 150-mg sample of tetrazole **18** in 100 mL of benzene was irradiated through a Corex filter sleeve for 2 h. Removal of the solvent under reduced pressure left a yellow oil which was purified by thick-layer chromatography using a 5:1 mixture of methylene chloride/ethyl acetate as the eluent. The major component isolated (96 mg, 74%) was a crystalline solid, mp 122–123 °C, whose structure was assigned as 2,4-dihydro-2-methyl[*l*]benzopyrano[4,3-*c*]pyrazole (**17**) on the basis of the following data: IR (neat) 6.15, 6.30, 6.40, 6.85, 7.20, 8.20, 8.45, 9.10, 9.55, 10.20, 11.85, 13.20 μm; UV (95% ethanol) 298 nm (ε 6190), 263 (9000), 254 (9220); NMR ($CDCl_3$, 60 MHz) τ 6.15 (s, 3 H), 4.80 (s, 2 H), 2.20–3.27 (m, 4 H), 2.70 (s, 1 H); MS *m/e* 186 (M^+), 185 (base), 160.

Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.05. Found: C, 70.82; H, 5.70; N, 14.85.

The structure of benzopyrano[4,3-*c*]pyrazole **17** was further confirmed by an independent synthesis involving the oxidation of 2,3,3a,4-tetrahydro-2-methyl[*l*]benzopyrano[4,3-*c*]pyrazole (**16**) with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). A mixture of 70 mg of **16** and 100 mg of DDQ in 5 mL of benzene was allowed to reflux for 5 h. The solvent was removed under reduced pressure, and the dark residue was passed through a small neutral alumina column using benzene/chloroform as the eluent to give **17** as the major product. The infrared and NMR spectra of this compound were identical in all respects with those of a sample of **17** obtained from the irradiation of tetrazole **18**.

Preparation of *N*-(*o*-Allyloxybenzoyl)-*N'*-phenylhydrazine. A sample of *o*-(allyloxy)benzoic acid[38] was converted to the corresponding acid chloride by stirring with excess thionyl chloride at room temperature for 24 h. To a 6.1-g sample of this acid chloride in 100 mL of methylene chloride was added 1 equiv of sodium *p*-nitrophenoxide (prepared by the addition of sodium hydride to 4.3 g of *p*-nitrophenol in 100 mL of ether). The solution was allowed to reflux for 24 h. At the end of this time, 10 mL of 95% ethanol was added followed by water. The organic extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 6.5 g (71%) of *p*-nitrophenyl (*o*-allyloxy)benzoate, mp 62–63 °C. A mixture containing 3.27 g of the above *p*-nitrobenzoate and 2.36 g of phenylhydrazine in 150 mL of tetrahydrofuran was heated at reflux for 17 h. At the end of this time the mixture was taken up in ether and washed with water. The organic layer was extracted with a 10% sodium hydroxide solution, followed by a washing with a saturated sodium chloride solution. The extracts were dried over magnesium sulfate and concentrated under reduced pressure to 2.71 g of an orange oil. This material was purified by silica gel chromatography using a 1:1 ether/pentane mixture as the eluent. The major function contained 1.94 g (66%) of *N*-(*o*-allyloxybenzoyl)-*N'*-phenylhydrazine as a crystalline solid: mp 73–74 °C; IR (KBr) 2.94, 3.03, 5.99, 6.23, 6.68, 7.62, 7.99, 8.51, 8.96, 9.97, 10.61, 10.86, 13.20, 14.37 μm; NMR ($CDCl_3$, 60 MHz) τ 5.32 (d, 2 H, *J* = 6.0 Hz), 4.40–4.80 (m, 2 H), 3.6–4.24 (m, 1 H), 3.84 (broad s, 1 H, exchanged with D_2O), 2.4–3.2 (m, 8 H), 1.80 (dd, 1 H, *J* = 6.0, 2.0 Hz), 0.51 (broad s, 1 H, exchanged with D_2O).

Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.55; H, 6.02; N, 10.44.

Treatment of 1-(*o*-Allyloxyphenyl)-*N*-(phenylhydrazidoyl) Chloride with Triethylamine. To a solution containing 1.52 g of *o*-allyloxybenzoylphenylhydrazine in 50 mL of ether was added 1.30 g of phosphorus pentachloride. The mixture was heated at reflux for 14 h, and then 1.9 g of phenol was added to destroy the phosphorus oxychloride. The resulting mixture was concentrated under reduced pressure, and 50 mL of benzene was added. To the above mixture was added 2 mL of triethylamine, and the resulting mixture was allowed to reflux for 2 h. At the end of this time the mixture was washed with a 0.5 N hydrochloric acid solution and water and then dried over magnesium sulfate. Removal of the solvent under reduced pressure

left 4.8 g of an orange residue which was chromatographed on silica gel and recrystallized from ether/pentane to give 0.86 g (61%) of 2,3,3a,4-tetrahydro-2-phenyl[*l*]benzopyrano[4,3-*c*]pyrazole (**20**) as a crystalline solid: mp 99–100 °C; IR (KBr) 6.23, 6.64, 6.73, 6.85, 7.15, 7.27, 7.58, 8.08, 8.23, 8.85, 9.12, 9.33, 9.62, 9.83, 9.93, 10.53, 11.84, 13.42, 14.45 μm; NMR ($CDCl_3$, 60 MHz) τ 5.76–7.02 (m, 4 H), 5.40 (dd, 1 H, J = 10.0, 5.0 Hz), 2.6–3.3 (m, 8 H), 2.20 (m, 1 H); MS *m/e* 250 (M^+, base), 249, 91, 77; UV (95% ethanol) 363 nm (ε 17 400), 304 (4900), 255 (13 000).

Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 77.06; H, 5.85; N, 11.33.

Preparation of Ethyl 2-[*o*-(Allyloxy)phenylhydrazono]-2-chloroacetate (21). To a mixture containing 8.79 g of *o*-allyloxyaniline[39] in 25 mL of a 3.0 N hydrochloride acid solution was added 1.18 g of sodium nitrite at 0 °C. After 15 min, solid sodium bicarbonate was added until the solution became basic and then 1.47 g of sodium acetate was added at 0 °C. To the above mixture was added 1.45 g of 2-chloroethyl acetoacetate, and the solution was allowed to stir at 25 °C for 90 min. The aqueous solution was extracted with ether, dried over magnesium sulfate, and concentrated under reduced pressure to give a dark oil. This material was passed through a column of neutral alumina to give 2.23 g (88%) of ethyl 2-[*o*-(allyloxy)phenylhydrazono]-2-chloroacetate (**21**): mp 41–42 °C (lit.[26] mp 42 °C); NMR ($CDCl_3$, 60 MHz) τ 8.62 (t, 3 H, J = 7.0 Hz), 5.60 (q, 2 H, J = 7.0 Hz), 5.40 (dt, 2 H, J = 5.0 Hz), 4.40–4.85 (m, 2 H), 3.6–4.23 (m, 1 H), 2.95–3.20 (m, 3 H), 2.40–2.60 (m, 1 H), 1.16 (broad s, 1 H).

Anal. Calcd for $C_{13}H_{15}N_2O_3Cl$: C, 55.23; H, 5.35; N, 9.91. Found: C, 55.29; H, 5.37; N, 9.97.

Treatment of Ethyl 2-[*o*-(Allyloxy)phenylhydrazono]-2-chloroacetate (21) with Triethylamine. To a solution containing 1.20 g of the above hydrazonochloroacetate **21** in 50 mL of benzene was added 2 mL of triethylamine. The solution was heated at reflux for 24 h, cooled, and taken up in ether. The organic layer was washed with a 0.5 N hydrochloric acid solution, dried over magnesium sulfate, and concentrated under reduced pressure to give 0.86 g (82%) of 2-carboethoxy-3,3a-dihydro-4*H*-pyrazolo[5,1-*c*][1,4]benzoxazine (**22**) as pale yellow crystals: mp 105–106 °C (lit.[26] mp 101 °C); IR (KBr) 5.80, 6.40, 6.70, 6.85, 7.73, 8.08, 8.90, 9.13, 9.53, 9.88, 10.68, 11.91, 12.88, 13.40, 13.80 μm; NMR ($CDCl_3$, 100 MHz) τ 8.64 (t, 3 H, J = 6.0 Hz), 7.10 (dd, 1 H, J = 18.0, 6.5 Hz), 6.66 (dd, 1 H, J = 18.0, 11.5 Hz), 6.44 (t, 1 H, J = 12.0 Hz), 5.54–5.90 (m, 4 H), 2.96–3.10 (m, 3 H), 2.40–2.50 (m, 1 H); MS *m/e* 246 (M^+, base), 218, 173, 133, 118, 105, 78; UV (95% ethanol) 345 nm (ε 11 200), 240 (5000).

Anal. Calcd for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.35; H, 5.75; N, 11.37.

Preparation of 1-(*o*-Allylphenyl)-*N*-(phenylhydrazidoyl) Chloride (23). To a solution containing 1.83 g of *o*-allylbenzoyl chloride in 50 mL of ether was added 1.1 g of phenylhydrazine at 0 °C. The reaction mixture was allowed to warm to room temperature, and then 50 mL of a 1.0 M sodium hydroxide solution was added. The ethereal layer was separated, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 2.11 g (82%) of *N*-(*o*-allylbenzoyl)-*N'*-phenylhydrazine: mp 158–159 °C; IR (KBr) 3.02, 6.07, 6.26, 6.67, 6.96, 7.61, 8.06, 10.10, 10.82, 13.31, 14.50 μm; NMR ($CDCl_3$, 60 MHz) τ 6.39 (d, 2 H, J = 6.0 Hz), 4.76–5.18 (m, 2 H), 3.60–4.50 (m, 1 H), 2.4–3.4 (m, 6 H).

Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.18; H, 6.40; N, 11.12.

To a solution containing 550 mg of the above benzoylhydrazine in 30 mL of ether was added 420 mg of phosphorus pentachloride. The mixture was heated at reflux for 14 h. The solvent was partially removed under reduced pressure, and 575 mg of phenol in 30 mL of benzene was added in order to destroy excess phosphorus pentachloride. The mixture was heated at 70 °C for 2 h and concentrated under reduced pressure to give hydrazidoyl chloride **23** as a pale yellow oil which was immediately reacted with triethylamine. The IR spectrum of **23** contained signals at 6.23, 6.70, 6.90, 7.42, 7.85, 9.25, 9.60, 10.90, 13.05, and 13.25 μm.

Treatment of 1-(*o*-Allylphenyl)-*N*-(phenylhydrazidoyl) Chloride (23) with Triethylamine. To a 500-mg sample of the above hydrazidoyl chloride in 30 mL of benzene was added 2 mL of triethylamine. The mixture was heated at 70 °C for 10 h, extracted with ether, washed with a 0.5 N hydrochloric acid solution, and dried over magnesium sulfate. The solvent was concentrated under reduced pressure, and the crystalline residue was recrystallized from ether/pentane to give 280 mg (60%) of 2,3,3a,4-tetrahydro-2-phenylindeno[1,2-*c*]pyrazole (**24**): 172–173 °C; IR (KBr) 6.23, 6.65, 6.81, 7.23, 7.53, 7.91, 8.46, 8.54, 9.12, 9.47, 9.66, 9.95, 10.40, 10.81, 11.24, 12.02, 13.28, 13.65, 14.35 μm; UV (methanol) 345 nm (ε 15 100), 250 (13 800); NMR ($CDCl_3$, 270 MHz) τ 7.29 (dd, 1 H, J = 15.4, 7.3 Hz), 6.92 (dd, 1 H, J = 14.3, 9.6 Hz), 6.74 (dd, 1 H, J = 15.4, 8.8 Hz), 6.39 (m, 1 H), 5.71 (t, 1 H, J = 9.6 Hz), 3.24 (t, 1 H, J = 6.0 Hz), 2.70–3.0 (m, 7 H), 2.3–2.40 (m, 1 H); MS *m/e* 234 (M^+), 134, 133, 131, 120, 116, 105, 91, 77.

Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 82.04; H, 6.04; N, 11.93.

A 94-mg sample of the above compound in 15 mL of benzene which contained 100 mg of chloranil was allowed to reflux for 48 h. At the end of this time the reaction mixture was washed with a 5% sodium hydroxide solution. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to give 91 mg (98%) of 2,4-dihydro-2-phenylindeno[1,2-*c*]pyrazole (**25**) as a crystalline solid: mp 100–101 °C; IR (KBr) 6.28, 6.73, 6.88, 7.30, 9.17, 9.38, 9.60, 9.93, 10.53, 12.48, 13.02, 13.30, 13.68, 14.67 μm; NMR ($CDCl_3$, 60 MHz) τ 6.35 (s, 2 H), 2.0–2.9 (m, 10 H); MS *m/e* 232 (M^+, base), 218, 161, 155, 77.

Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 83.05; H, 5.27; N, 11.68.

Acknowledgment. We wish to thank the National Cancer Institute, DHEW (CA-12195), for generous support of this work. Aid in the purchase of the NMR spectrometer (XL-100) used in this work was provided by the NSF via an equipment grant.

Registry No.—**1**, 65103-32-4; **2**, 65103-33-5; **3**, 65103-34-6; **4**, 65103-35-7; **5**, 65103-36-8; **6**, 65103-37-9; **7**, 65103-38-0; **8**, 23894-57-7; **9**, 65103-39-1; **10**, 65103-40-4; **11**, 65103-41-5; **13**, 65103-42-6; **14**, 65103-43-7; **15**, 65103-44-8; **16**, 65103-45-9; **17**, 65103-46-0; **18**, 65103-23-3; **19**, 65103-47-1; **20**, 65103-48-2; **21**, 61364-10-1; **22**, 61364-13-4; **23**, 65103-22-2; **24**, 2380-43-0; **25**, 65103-24-4; 5-phenyltetrazole, 18039-42-4; 5-bromo-1-pentene, 1119-51-3; dimethyl acetylenedicarboxylate, 762-42-5; 5-chloro-1-pentyne, 14267-92-6; 1-(4-pentynyl)-5-phenyltetrazole, 65103-25-5; methyl acrylate, 96-33-3; 1-(4-pentynyl)-3-phenyl-5-carbomethoxypyrazole, 65103-26-6; 4-bromo-1-butene, 5162-44-7; 5-phenyltetrazole silver salt, 65103-27-7; allyl bromide, 106-95-6; 5-(*o*-hydroxyphenyl)tetrazole, 51449-77-5; methyl iodide, 74-88-4; 2-methyl-5-(*o*-hydroxyphenyl)-tetrazole, 65103-28-8; propargyl bromide, 106-96-7; *N*-(*o*-allyloxybenzoyl)-*N'*-phenylhydrazine, 65103-29-9; *o*-(allyloxy)benzoic acid, 59086-52-1; *o*-allylbenzoyl chloride, 52542-42-4; β-nitrophenyl (*o*-allyloxy)benzoate, 65103-30-2; phenylhydrazine, 100-63-0; *o*-allyloxyaniline, 27096-64-6; *N*-(*o*-allylbenzoyl)-*N'*-phenylhydrazine, 65103-31-3.

References and Notes

(1) Photochemical Transformations of Small Ring Heterocyclic Compounds. 96. For Part 95, see A. Padwa, T. J. Blacklock, D. Getman, N. Hatanaka, and R. Loza, *J. Org. Chem.*, in press.
(2) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963).
(3) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes", S. Patai, Ed., Interscience, London, 1964, pp 806–878.
(4) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968); **41**, 403 (1976).
(5) R. Huisgen, R. Sustmann, and K. Bunge, *Chem. Ber.*, **105**, 1324 (1972).
(6) A. Padwa and P. H. J. Carlsen, *J. Am. Chem. Soc.*, **97**, 3682 (1975); **98**, 2006 (1976); **99**, 1514 (1977).
(7) A. Padwa, A. Ku, A. Mazzu, and S. I. Wetmore, Jr., *J. Am. Chem. Soc.*, **98**, 1048 (1976).
(8) A. Padwa, P. H. J. Carlsen, and A. Ku, *J. Am. Chem. Soc.*, **99**, 2798 (1977).
(9) A. Padwa and N. Kamigata, *J. Am. Chem. Soc.*, **99**, 1871 (1977).
(10) L. Garanti, A. Vigevani, and G. Zecchi, *Tetrahedron Lett.*, 1527 (1976).
(11) G. LoVecchio, G. Grassi, F. Risitano, and F. Foti, *Tetrahedron Lett.*, 3777 (1973).
(12) J. S. Clovis, A. Eckell, R. Huisgen, and R. Sustmann, *Chem. Ber.*, **100**, 60 (1967).
(13) R. Huisgen, J. Sauer, and M. Seidel, *Chem. Ber.*, **94**, 2503 (1961).
(14) R. N. Butler, *Adv. Heterocycl. Chem.*, **21**, 323 (1977).
(15) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **7**, 321 (1968).
(16) R. N. Butler and F. L. Scott, *Chem. Ind. (London)*, 1216 (1970).
(17) F. R. Benson, *Heterocycl. Compd.*, **8**, 1 (1967).
(18) F. R. Benson, *Chem. Rev.*, **41**, 1 (1947).
(19) R. N. Butler, *Leicester Chem. Rev.*, **10**, 12 (1969).
(20) R. Raap and J. Howard, *Can. J. Chem.*, **47**, 813 (1969).
(21) B. Elpern and F. C. Nachod, *J. Am. Chem. Soc.*, **72**, 3379 (1950).
(22) R. R. Fraser and K. E. Haque, *Can. J. Chem.*, **46**, 2855 (1968).
(23) R. N. Butler, *Can. J. Chem.*, **51**, 2315 (1973).
(24) L. Garanti, A. Sala, and G. Zecchi, *Synthesis*, 666 (1975).
(25) R. Fusco, L. Garanti, and G. Zecchi, *Tetrahedron Lett.*, 269 (1974).
(26) L. Garanti, A. Sala, and G. Zecchi, *J. Org. Chem.*, **42**, 1389 (1977).
(27) For a review of intramolecular 1,3-dipolar cycloadditions, see A. Padwa, *Angew. Chem., Int. Ed. Engl.*, **15**, 123 (1976), and references cited therein.
(28) K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Am. Chem. Soc.*, **95**, 7301 (1973).
(29) We previously reported that the intramolecular 1,1-cycloaddition reaction

of 2-but-3-enyl-substituted nitrile ylides does not occur.[9] This was attributed to the stereoelectronic problem of locating the p orbital of the terminal olefin in the proper position for maximum overlap with the second LUMO of the nitrile ylide. A similar explanation would also account for the absence of a 1,1-cycloaddition reaction with tetrazole **4**.
(30) T. Sasaki, K. Kanematsu, and Y. Yukimoto, *J. Chem. Soc. C.*, 481 (1970); *J. Org. Chem.*, **36**, 813 (1971).
(31) While our studies were in progress, a report by Garanti, Sala, and Zecchi appeared[26] describing the 1,3-dipolar cycloaddition of hydrazonyl chloride **21**.
(32) P. Caramella and K. N. Houk, *J. Am. Chem. Soc.*, **98**, 6397 (1976).
(33) P. Caramella, R. W. Gandour, J. A. Hall, C. G. Deville, and K. N. Houk, *J. Am. Chem. Soc.*, **99**, 385 (1977).
(34) W. Kirmse in "Carbene Chemistry", Academic Press, New York, N.Y., 1964.
(35) K. N. Houk and R. W. Gandour, private communication.
(36) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by the Atlantic Microanalytical Laboratory. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear resonance spectra were determined at 60 MHz with a Varian T-60 spectrometer and at 100 MHz with a Varian XL-100 spectrometer.
(37) W. G. Finnegan, R. A. Henry, and R. Lofquist, *J. Am. Chem. Soc.*, **80**, 3908 (1958).
(38) A. Padwa, P. H. J. Carlsen, and A. Ku, *J. Am. Chem. Soc.*, in press.
(39) J. von Braun and O. Braunsdorf, *Ber.*, **54**, 685 (1921).

Reversible Interconversion of *N*-Nitroso(2-methylamino)acetonitrile and 3-Methyl-5-amino-1,2,3-oxadiazolium Chloride and Related Reactions[1]

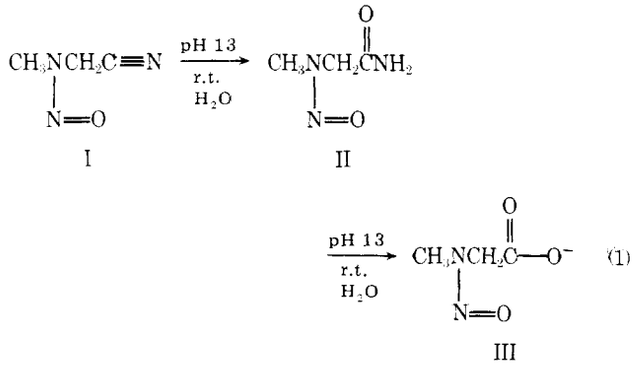
Saroj K. Vohra,[2] George W. Harrington, and Daniel Swern*

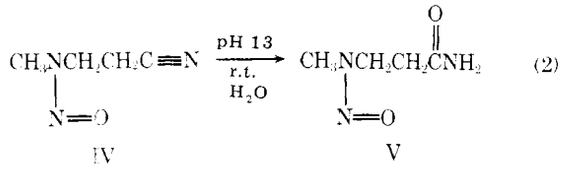
Department of Chemistry and Fels Research Institute, Temple University, Philadelphia, Pennsylvania 19122

Received August 11, 1977

Reaction of *N*-nitroso(2-methylamino)acetonitrile (I) with gaseous hydrogen chloride in dry methanol, ethanol, or ether is a fast reaction that yields 3-methyl-5-amino-1,2,3-oxadiazolium chloride (VI) virtually quantitatively. A pathway for the conversion of I to VI involving anchimeric assistance by the nitroso group is suggested. With aqueous base at pH 8–11, VI is reversibly converted to I, but at pH 11.5–14 VI is converted to *N*-nitrososarcosine (VII). Treatment of the homologous *N*-nitroso(3-methylamino)propionitrile (IV) with hydrogen chloride in methanol is a relatively slow reaction and does not yield a cyclic product; IV is denitrosated and converted to methyl (3-methylamino)propionate hydrochloride (VIII), with concomitant formation of ammonium chloride. The unnitrosated parent amine of I, methylcyanomethylamine hydrochloride (IX), on reaction with hydrogen chloride, behaves in the same manner as IV; products are methyl(2-methylamino)acetate hydrochloride (X) and ammonium chloride. A simple denitrosation procedure for *N*-nitrosamines derived from secondary amines is also described.

In an earlier paper,[3] we reported the unexpectedly rapid hydrolysis of *N*-nitroso(2-methylamino)acetonitrile (I) in aqueous alkaline solution under mild conditions (room temperature and pH 13) to a salt of *N*-nitrososarcosine (III) via the intermediate amide (II) (eq 1). The homologous *N*-nitrosamine, *N*-nitroso(3-methylamino)propionitrile (IV), was hydrolyzed to the amide (V) under similar conditions but at a rate only about 1/500 that of I (eq 2). These results, coupled with ^{18}O-labeling studies and determination of activation parameters, showed unequivocally that anchimeric assistance by the *N*-nitroso group plays the dominant role in the more rapid hydrolysis of I.

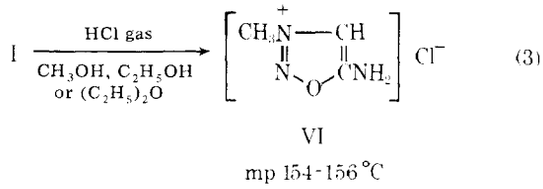




As part of our ongoing investigation of anchimeric effects of the *N*-nitroso group in conjunction with studies on structure–biological activity relationships in *N*-nitrosamines, we examined the behavior of I and IV with anhydrous hydrogen chloride in nonaqueous solvents—methanol, ethanol, and diethyl ether; the results of that study are reported here. During that investigation deuterium-exchange studies were conducted on starting materials and products with interesting results. Finally, a mild chemical denitrosation technique was developed for certain nitrosamines which should be useful in destroying carcinogenic or potentially carcinogenic nitrosamines.[4]

Results and Discussion

Treatment of I in dry methanol with hydrogen chloride gas for 1 h followed by solvent evaporation, washing with acetone, and recrystallization from ethanol yields 3-methyl-5-amino-1,2,3-oxadiazolium chloride (VI) in high to quantitative yield (eq 3). This compound had been prepared similarly in 1962 by Daeniker and Druey.[5] Similar results are obtained using ethanol or ether as solvent.



VI

mp 154–156 °C

Compound VI undergoes (a) typically *rapid* exchange of two protons by deuterium when D_2O is added to a Me_2SO-d_6 solution, (b) *slow* exchange of the vinyl proton when it remains in D_2O solution overnight, (c) complete reconversion to I on treatment with aqueous base at pH 8–11, and (d) complete

0022-3263/78/1943-1671$01.00/0