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CHEMISTRY OF GEMINAL DIAZIDES. REARRANGEMENTS TO N-CYANO COMPOUNDS

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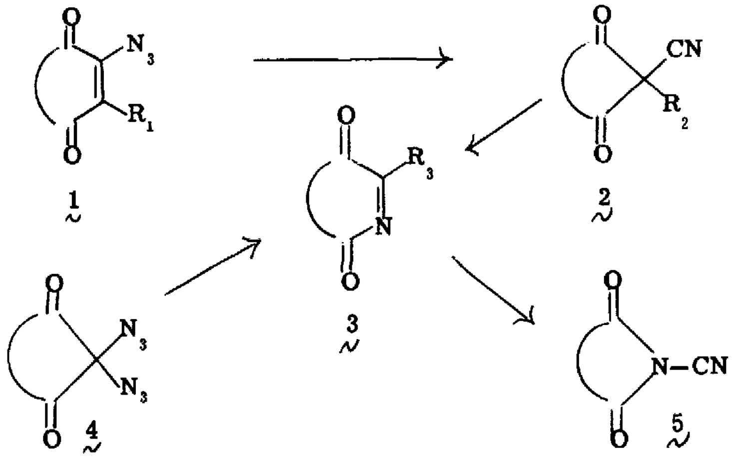
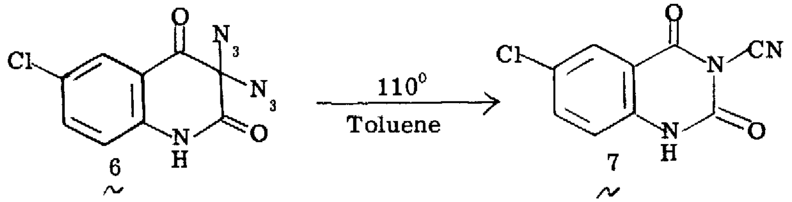
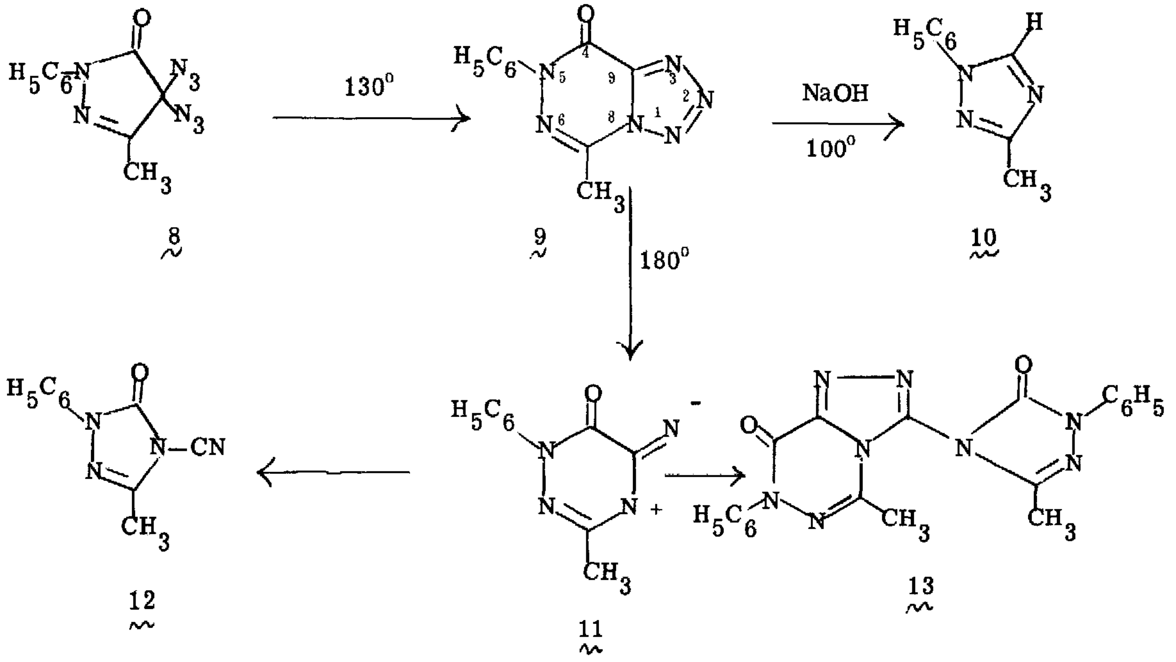
We have recently shown that certain 2-azido-2-ene-1,4-diones (azido-1,4-quinones) ring contract to 2-cyano-1,3-diones (2-cyano-1,3-cyclopentenediones) upon thermolysis, i.e., **1** → **2**.[1] Also, we have observed that cyclic 2-azido-1,3-diones (2-azido-2-cyano-1,3-cyclopentenediones) thermally ring expand to cyanoimines (cyanoazaquinones), i.e., **2** $R_2=N_3$ → **3** $R_3=CN$.[2] In fact, the transformation, **1** $R_1=N_3$ → **2** $R_2=N_3$ → **3** $R_3=CN$, can be accomplished directly upon thermolysis of certain 2,3-diazido-2-ene-1,4-diones (2,3-diazido-1,4-quinones).[2] Thus, this vicinal vinyl diazide rearrangement proceeds by an initial ring contraction followed by ring expansion with an overall interconversion of a nitrogen and carbon in the ring system. From these results, one would anticipate that cyclic geminal diazides such as 2,2-diazido-1,3-diones, **4**, would thermally ring expand to azidoimines (or tetrazoles)[3] **3** $R_3=N_3$ which are structurally analogous to **1** and thus should subsequently ring contract to N-cyanoimides, **5**. Therefore, the geminal diazide series should proceed by an initial ring *expansion followed by ring contraction where again an overall nitrogen and carbon interconversion* takes place. To test this, the geminal diazides **6** and **8** were prepared and their thermal chemistry investigated. This study did demonstrate such a rearrangement.



1,2,3,4-*H*-3,3-Diazido-6-chloro-2,4-dioxoquinoline (6) was obtained in 98% yield when an ethanolic solution of 3,3,6-trichloro-2,4-dioxoquinoline[4] was treated with aqueous sodium azide: mp, 140°dec; ir (Nujol, cm^{-1}) 3115, 2100, 1720, 1680; ^{1}H nmr (CDCl$_3$:DMSO-d$_6$ 4 : 1, δ) 11.35 b (1), 7.17-7.89 m(3); *anal.* C, 39.04; H, 1.57; N, 35.29. Thermolysis of this diazide in refluxing anhydrous toluene for 8 hrs. gave 1,2,3,4-H-6-chloro-3-cyano-2,4-dioxoquinazoline 7 in 49% isolated (silica gel chromtaography) yield: mp, 245° dec; ir (Nujol, cm^{-1}) 3050, 2160, 1665, 1635; ^{1}H nmr (CDCl$_3$:DMSO-d$_6$ 1:1, δ) 11.57 b(1), 7.28-7.88 m(3); mass spectrum (70 ev) 221, M^{+}; *anal.* C, 48.64; H, 1.80; N, 18.59. The ^{13}C nmr spectrum of a DMSO-d$_6$ solution of 7 showed absorptions (relative to TMS) for the nine carbons at δ, 184.5, 174.7, 158.9, 139.2 134.7, R 126.8, 124.1, 119.8, and 119.0. From T$_1$ experiments, the absorptions at 134.7, 124.1, and 119.0 can be assigned to the proton substituted aromatic carbons. The absorption at 119.8 is assigned to the N-cyano group. This is based upon the observation that the analogous functionality in N-cyanopyrrolidine has a chemical shift of α, 117.2



4,4-Diazido-3-methyl-1-phenylpyrazoline-5-one (8)[5] was prepared in 91% yield from the corresponding dichloride[6] upon treatment with ethanolic sodium azide; mp, 26-27°; ir (Nujol, cm^{-1}) 2095, 1730, 1720; ^{1}H nmr (CDCl$_3$, δ) 2.00 s (3), 7.07-7.93 m(5); *anal.* C, 47.41; H, 3.28; N, 44.05. Thermolysis of this diazide in refluxing chlorobenzene gave the tetrazole, 9, in 98% yield: mp, 192° dec; ir (Nujol, cm^{-1}) 1700, 1690, 1635; ^{1}H nmr (CDCl$_3$, δ) 2.93 s (3), 7.33-7.63 m (5); mass spectrum (70 ev) 228 M^{+}; *anal.* C, 52.86; H, 3.62; N, 36.94. This tetrazole is envisaged as arising from imine bond migration to one of the azide nitrogens followed by intramolecular 1,3-dipolar cycloaddition of the remaining azide moiety to the conjugated imine bond. From literature precedents[7] one might anticipate carbonyl migration rather than imine migration. However, base hydrolysis of 9 resulted in its unusual transformation to 1-phenyl-3-methyl-1H, 2,4-triazole[8] (10) (98%) which is consistent with an imine carbon to itrogen bond at positions -7 and -8 in the tetrazole 9.



Subsequent thermolysis of 9 in refluxing o-dichlorobenzene gave the N-cyano compound 12 (43%) and an unsymmetrical dimer (44%) which is tentatively assigned structure 13. The ring contracted compound is viewed as arising from the iminonitrene 11 and the dimer from 1,3-dipolar cycloaddition of the nitrene to the cyano group of 12. The regiochemistry of this cycloaddition is clearly not established but is based upon analogy with *previously reported cycloadditions* of iminonitrenes to phenylnitrile.[9]

The structure of 12 is based upon the following characteristic properties: mp, 140-142°; ir (Nujol, cm^{-1}) 2250, 1760, 1625, 1590; ^1H nmr ($CDCl_3$, δ) 2.40 s(3), 7.13-7.73 m(5); mass spectrum (70 ev) 200 $M^{\dot{+}}$; anal. C, 59.64; H, 4.07; N, 28.68. Structural data for the dimer are: mp, 214-221°; ir (Nujol, cm^{-1}) 1765, 1720, 1625, 1600; ^1H nmr ($CDCl_3$, δ) 2.50 s(3), 2.70 s(3), 7.43 ts (5), *7.13-8.10 m (5); molecular wt, 400 (chemical ionization mass spectrum); mass* spectrum (70 ev) identical to that of 12; anal. C, 59.83, H, 3.94, N, 27.88. The most revealing of the above data are the pmr spectrum which shows the dimer to be unsymmetrical, and the electron impact mass spectrum which is virtually identical to that of 12. Such would be anticipated *if the dimer undergoes a retrocycloaddition to 11 and 12 upon electron impact.*

ACKNOWLEDGEMENT

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