been observed to generate light during electrogenerated chemiluminescence.[10] An important key feature of this new chemiluminescent mechanism is the rapid chemical reaction of what was a very easily reduced compound to form a strongly reducing species within the solvent cage. Return of an electron to the radical-cation form of the initial electron donor then results in excited-state generation. Preliminary evidence that the path leading to light generation occurs within the solvent cage comes from the observation of the effect of added trap molecules. Thus, saturating the chemiluminescing solution with O_2 results in only a small decrease in light emission due to quenching of the singlet state of the aromatic hydrocarbon. Also, the addition of tetramethylethylene does not divert the radical-ion intermediates leading to light generation.

The total yield of electronically excited states for this reaction should be sensitive to a number of factors such as the nature of the hydrocarbon, the rate of decarboxylation, the cage lifetime, the solvent polarity, and the excited-state yield on back-electron transfer. We have compared the chemiluminescence of **1** with perylene to tetramethyldioxetane.[11] Preliminary results indicate that for this system the yield of photons is ~10 ± 5%. Thus, even though the reaction has not been optimized, the light yield is remarkably high.

Several previously reported chemiluminescent reactions appear to be proceeding by the proposed electron exchange machanism. The well-known oxalate ester system is reported to be "catalyzed" by aromatic hydrocarbons.[13] Chemiluminescence from α-peroxylactones appears to be strongly dependent upon the nature of the aromatic hydrocarbon.[14] The reaction of phthaloyl peroxide almost certainly proceeds by a similar mechanism.[15] Our recent report of chemiluminescence from a suspected cyclic diacyl peroxide fits this interpretation.[16] Chemically initiated electron-exchange luminescence may be a general phenomenon responsible for many chemi- and bioluminescent reactions. Further efforts to unravel the details of these chemiluminescent processes and probe the generality of this mechanism are underway.

Acknowledgment. We wish to thank Professor Faulkner of this department for the determination of the reduction potential of benzocoumarin and for many helpful discussions. This work was supported in part by the Office of Naval Research and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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Ja-young Koo, Gary B. Schuster* [18]
Department of Chemistry, Roger Adams Laboratory
University of Illinois, Urbana, Illinois 61801

Received May 27, 1977

Novel Cyclization of Allyldiazomethane to 3-Methyl-3*H*-pyrazole[1]

Sir:

Among the large number of intramolecular cyclizations of diazoalkenes which afford formal 1,3-dipolar cycloaddition products such as pyrazoles or pyrazolines, those of allyldiazomethanes are apparently unknown. Allyldiazomethanes generally decompose thermally[2] or photochemically[3] to form carbene-type reaction products, or in some case cyclize intermolecularly[4] rather than intramolecularly. Herein we wish to report a novel example of the cyclization of an allyldiazomethane derivative through an unprecedented process which represents a notable exception to the generally observed reaction modes.

When the sodium salt of α-(1,3,5-cycloheptatrien-3-yl)-acetophenone tosylhydrazone (**1**, mp 129 °C)[5] was decomposed in dry diglyme at 145 °C, the reaction mixture immediately turned red as sodium toluenesulfinate was liberated, and 10-phenyl-1,11-diazatricyclo[6.3.0.0^{4,6}]undeca-2,8,10-triene (**2**, mp 57 °C) was isolated (Scheme I) in 66% yield (ν_{max}^{KBr} 3050, 1650, 1554 cm^{-1}; λ_{max} 277 nm (log ϵ 4.33) in cyclohexane; *m/e* 222 (M^+, 100%), 221, 207, 194, 157, 128, 104). The ^1H NMR spin decoupling and the observance of a 5% NOE between the exo-C(7)-H and C(9)-H proton provide an unequivocal assignment for all the hydrogens of **2**. This assignment was further supported by the close similarity of its ^{13}C NMR spectrum[6] to that of 1,10-diazatricyclo[5.3.0.0^{4,6}]deca-2,7,9-triene[7] recently reported by Dreiding and coworkers (^{13}C NMR spectrum of **2** (δ units in $CDCl_3$), C(2), 128.0 (d); C(3), 120.1 (d); C(4), 13.0 (d); C(5), 9.6 (t); C(6), 22.1 (d); C(7), 26.7 (t); C(8), 135.4 (s); C(9), 104.5 (d); C(10), 144.9 (s)).

Scheme I

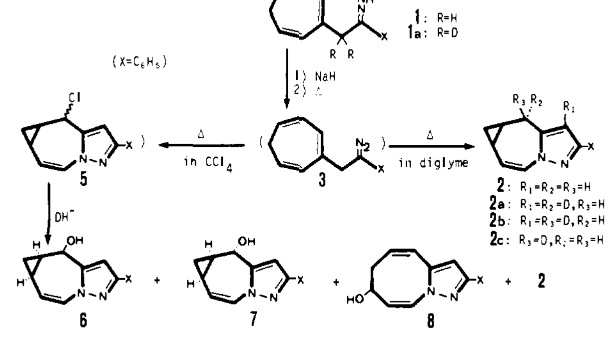
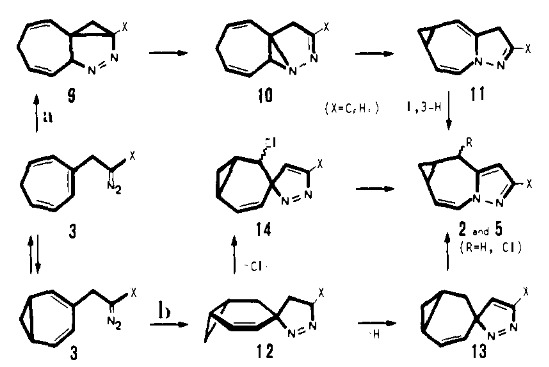


Table I. Nuclear Magnetic Resonance Spectra[a] of **2**, **6**, **7**, and **8**

Compd	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(9)
2	6.68 $J_{23} = 9.5$	5.53 $J_{34} = 5.3$	1.19 $J_{45} = 9.0$ (exo) $J_{45} = 4.5$ (endo)	0.67 (exo), 0.41 (endo) $J_{ab} = 4.5$ $J_{56} = 7.8$ (exo) $J_{56} = 5.3$ (endo)	1.45 $J_{46} = 8.6$	3.19 (exo), 2.59 (endo) $J_{ab} = 15.4$ $J_{67} = 3.8$ (exo) $J_{67} = 7.0$ (endo)	6.24
6	6.72 $J_{23} = 9.3$	5.62 $J_{34} = 7.5$	1.40 J_{45} (exo)[b] J_{45} (endo)[b]	0.89 (exo), 0.90 (endo) $J_{ab} = 5.2$ $J_{56} = 9.2$ (exo) $J_{56} = 5.7$ (endo)	2.00 $J_{46} = 8.0$	5.19 (exo), OH (endo) $J_{67} = 2.0$ (exo)	6.65
7	6.77 $J_{23} = 9.0$	5.72 $J_{34} = 6.0$	1.45 $J_{45} = 8.1$ (exo) $J_{45} = 5.7$ (endo)	1.03 (exo), 0.67 (endo) $J_{ab} = 5.1$ $J_{56} = 9.0$ (exo) $J_{56} = 5.5$ (endo)	1.96 $J_{46} = 8.1$	OH (exo), 5.08 (endo) $J_{67} = 5.9$ (endo)	6.51
8	6.90 $J_{23} = 9.0$	5.80 $J_{34} = 6.0$	4.80	2.60 $J_{56} = 5.0$	6.00 $J_{67} = 12.0$	6.50	6.50

[a] Chemical shift in δ units; coupling constant in hertz; solvent, $CDCl_3$. [b] Coupling constants could not be read clearly.

Scheme II



Thermolysis of the isomeric α-(1,3,5-cycloheptatrien-1-yl)acetophenone tosylhydrazone (**4**, mp 152 °C), on the other hand, afforded two carbene-type products, α-(1,3,5-cycloheptatrien-1-yl)styrene and 1-styrylcycloheptatrine in 16 and 30% yields, respectively. Although no intermediate could be isolated from the decomposition of **1**, the intermediacy of the initially formed diazo compound **3** was substantiated by the suppression of the red coloration and the formation of α-(1,3,5-cycloheptatrien-3-yl)acetophenone hydrazone[8] when the sodium salt of **1** was decomposed in the presence of tri-*n*-butylphosphine.[9] The following experiments were carried out in order to help elucidate the relationship between the structure of **2** and the reaction pathway. Vacuum pyrolysis of the dry sodium salt of the dideuterio analogue **1a** was carried out at 150 °C (0.05 mmHg) and the product composition was found to contain a mixture of dideuterio **2a** (54%), **2b** (43%), and monodeuterio **2c** (4%) by ^{1}H NMR analysis. Pyrolysis of **1a** in dry diglyme at 145 °C afforded a mixture of **2a** (24%), **2b** (22%), and **2c** (54%). Similar results were obtained in dry toluene at 110 °C where a mixture of **2a** (32%), **2b** (23%), and **2c** (45%) was obtained. The above results reveal that the side-chain hydrogen in **3** must shift to the C(7) position in **2**. In addition, the formation of a considerable amount of **2c** in solution suggests that an intermolecular hydrogen abstraction via a radical species competes with the intramolecular hydrogen shift. This ambiguity was further clarified by the decomposition of the dry sodium salt of **1** in refluxing carbon tetrachloride which afforded four products, **6** (benzoate mp 134 °C), **7** (benzoate mp 111 °C), **8** (benzoate mp 84 °C), and **2** in 6, 17, 2, and 9% yields, respectively. The structures of the three alcohols were determined by their ^{1}H NMR spectra (see Table I) and their formation is best rationalized by the facile hydrolysis of the unstable chldride **5** which leads to a cyclopropylcarbinyl cation.[10] Evidence that the C(7) position is substituted both with hydrogen and chlorine atoms and is dependent on the solvent is intriguing and inconsistent with an ionic pathway.

Two intrinsically different pathways, a and b, can be considered for the formation of **2** (Scheme II). Path a,[11] however, does not accommodate the formation of the three alcohols (**6**, **7**, and **8**) in carbon tetrachloride. Furthermore, the thermal transformation[13] of **9** to **10** would be unlikely to occur, considering the general reaction modes of diazabicyclo[3.1.0]hexenes which involve nitrogen extrusion[14] to form a carbene or a diradical, retro-1,3-dipolar addition[15] and isomerization[16] to a pyridazine derivative. The most likely path to account for the formation of **2** and **5** as well as the labeling experiments involves the formation of a spiro 1,4 diradical **12** (path b) in which the two radical centers are located in opposite rings and are twisted at nearly 90° and thus are noninteracting.[17] Collapse of this diradical in diglyme or toluene results in the formation of **13** either by disproportionation between the two radical sites or by an intermolecular hydrogen abstraction. In carbon tetrachloride, however, the cyclopropylcarbinyl radical function[18] abstracts a chlorine atom to form **14**. The formations of **2** and **5** can then be rationalized in terms of the van Alphen rearrangement[19] of **13** and **14**.

Huisgen[20] has pointed out as chemical evidence to rebut the Firestone diradical mechanism[21] that neither abstraction nor disproportionation of an intermediate diradical has been observed in any 1,3 dipole + dipolarophile system. Thus, the generation of **12** and its chemical behavior is intriguing in view of the reactivity of diazoalkanes as 1,3 dipoles.[22] Further studies are in progress to establish the generality of this novel cyclization.

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H, m), 5.8–6.2 (2 H, m), 6.3–6.5 (1 H, m); *m/e* 326 (M^+), 311, 236, 221, 208, 118, 105, 104, 103,

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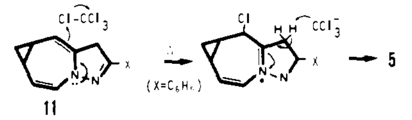
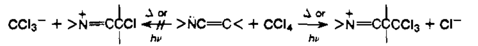
Scheme III





$$CCl_3^- + >\overset{+}{N}{=}C\text{C}Cl \underset{h\nu}{\overset{\Delta\text{ or}}{\not\leftarrow}} >\ddot{N}C{=}C< + CCl_4 \underset{h\nu}{\overset{\Delta\text{ or}}{\longrightarrow}} >\overset{+}{N}{=}C\text{C}CCl_3 + Cl^-$$

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Tsutomu Miyashi, Yoshinori Nishizawa
Takekatsu Sugiyama, Toshio Mukai*
Department of Chemistry, Faculty of Science
Tohoku University, Sendai, 980 Japan

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Regiospecific Anodic Cyanation of Pyrroles and Indoles

Sir:

I wish to report here that pyrrole cyanides are directly generated in high yield from pyrroles by an anodic process. The results obtained reveal a unique and potentially useful reaction which should be general for nitrogen heterocycles. Pyrrole cyanides are in general obtained from Mannich bases or aldoximes, but most of the reported routes are tedious to carry out and of poor yield in some cases.[1]

It was at first anticipated that, if the anodic oxidation of pyrroles is conducted in methanolic cyanide solution, a 1,4 addition of cyano and/or methoxy group to pyrrole ring would be observed to produce 3-pyrrolines, by analogy with our previous results of anodic cyanomethoxylation of 2,5-dimethylfuran and thiophene.[2] However, substitution products were exclusively formed.

The procedure is described for the conversion of 1-methylpyrrole to 1-methylpyrrole-2-carbonitrile. The reaction was performed at a controlled anode potential of 1.0 V vs. SCE, in a divided cell with platinum plate electrodes having an area of 8 cm^2 and a magnetic stirrer bar in the anode compartment, at room temperature, in methanolic sodium cyanide solution (organic substrate, 0.4 M; cyanide, 0.8 M). The oxidation was terminated after passage of 2 F/mol of added pyrrole. The anolyte was worked up by distillation of the methanol. Then, saturated aqueous NaCl was added and the mixture extracted in ether. The ethereal solution was dried over anhydrous magnesium sulfate, filtered, and evaporated, and the residual oil was distilled under reduced pressure (bp 101–103 °C (27 mmHg)). The distillate consisted of a single component. The product was identified by IR, mass, and NMR spectroscopy to be 1-methylpyrrole-2-carbonitrile, 64% yield. Anal. Calcd for $C_6H_6N_2$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.94; H, 5.68; N, 26.40.

Table I summarizes the results of electrochemical reactions using other compounds. All products were identified by the elemental and spectroscopic analyses and by comparison with the authentic samples prepared by other routes. One major advantage of the present reaction lies in its high selectivity with regard to the position of attack. VPC of the reaction product generally showed a single peak. The product yields from 1-phenylpyrroles are superior to those from 1-methylpyrroles. Cyanation of indoles occurs exclusively on the pyrrole part of the indole molecule. The reaction point of 1-methylindole in the present nucleophilic substitution is intriguing: electrophilic substitution usually occurs at position 3,[3] while the present anodic cyanation predominantly takes place on position 2. The alkyl or aryl group at the 1 position is not attacked. The current efficiency for the formation of pyrrole cyanides increases with decreasing amounts of passed electricity. Methoxylation, which is often observed as side reaction in the anodic oxidation in methanolic cyanide solution, was suppressed completely. Isocyanation was not observed.

At the potential adopted only organic substrates are oxidized to produce cation radical intermediates.[2a] If the reaction of the

Scheme I