large molecules of this type by IETS. Our current effort focuses on studying chemical derivatives of these type of surface-bonded structures.

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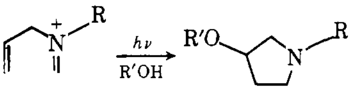
Photochemistry of *N*-Allyliminium Salts. A Novel Photocyclization Reaction Leading to Pyrrolidines

Sir:

The photochemistry of unsaturated hydrocarbons containing nonconjugated π chromophores linked through saturated carbon chains remains as one of the more interesting areas of organic chemistry. The number of unique molecular transformations observed have served as the basis for elucidation of the mechanistic details of excited-state reactions and for the synthetic utility of organic photochemistry. The di-π-methane rearrangement,[1] which transforms compounds containing the 1,4-pentadiene grouping to vinylcyclopropanes, and intramolecular [2 + 2] cycloaddition reactions of 1,5-hexadienes and higher homologues[2] stand as exceptionally general examples of this point. Our interest in this area of photochemistry led recently to an exploration of the excited-state chemistry of compounds containing the *N*-allyliminium salt functionality (**1**) in which one of the two nonconjugated π moieties is part of the imine (C═N) group. We wish to report the preliminary results of this investigation which demonstrate that these systems undergo a novel cyclization process to produce pyrrolidines, a reaction of potential synthetic and mechanistic interest.



1 **2**

Initial investigations were conducted using the 5-phenyl-2-isobutenyl-1-pyrrolinium salts, **10** and **11**, prepared by sequences starting with the known[3] 2,4,4-trimethyl-1-pyrroline 1-oxide (**3**). Isobutenylmagnesium bromide[4] was added to **3** (THF, reflux) to produce the hydroxylamine **4** (70%, mp 42–44 °C)[5] which was converted to the nitrone **8** (HgO, $CHCl_3$, 98%). Addition of phenylmagnesium bromide to **8** (Et_2O, reflux) gave the 5-phenyl-1-hydroxypyrrolidine **5**[6a] which was subsequently reduced ($LiAlH_4$, $AlCl_3$, Et_2O, 96%) to pyrrolidine **6** and chlorinated (NCS, Et_2O, 100%) furnishing the *N*-chloramine **7** as a mixture of diastereomers.[6b] Dehydrochlorination was performed using methanolic KOH and provided the 5-phenyl-2-isobutenyl-1-pyrroline (**9**, 72% after silica gel chromatography). The tetramethyl-1-pyrrolinium perchlorate **10** (mp 126–127 °C) was derived from **9** by reaction with methyl iodide (EtOH, reflux) followed by perchlorate anion exchange (Dowex 1-X8, 38%). Generation of the protonated 1-pyrrolinium salt **11** was performed prior to irradiation by addition of 70% aqueous $HClO_4$.[7]

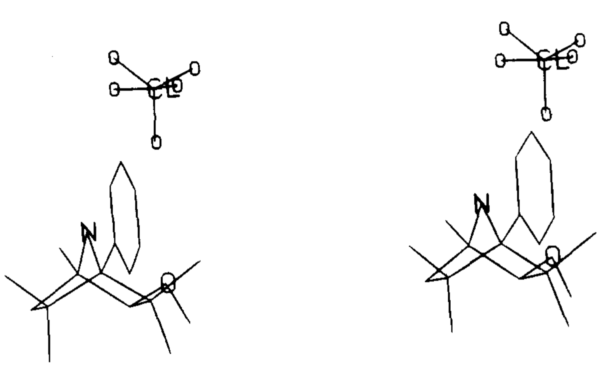
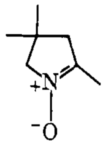


Figure 1. Unretouched photograph of stereodisplay of atomic coordinates and connectivity of the ammonium perchlorate derivative of **12**, taken on a Vector General Graphic System, programmed by S. M. Swanson and C. Morimoto. All unlabeled atoms are carbons. The perchlorate ion is shown as it appears with inversion disorder.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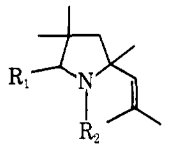
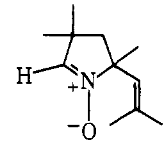

4, R_1 = H; R_2 = OH
5, R_1 = Ph; R_2 = OH
6, R_1 = Ph; R_2 = H
7, R_1 = Ph; R_2 = Cl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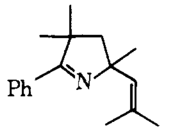
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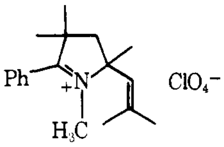
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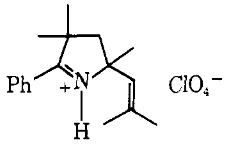
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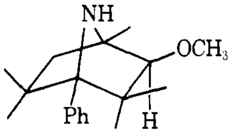
Irradiation of a solution of **11** (4.3 mM, from **9** and 2 equiv of $HClO_4$) in methanol using Corex-filtered light[8a] led to consumption of the starting material and simultaneous production of a major photoproduct **12** which was isolated in pure form (44%)[8b] by neutralization (saturated $NaHCO_3$) and concentration of the photolysate followed by silica gel TLC (50% Et_2O-hexane). Identification of **12** as 1,3,3,5,5-pentamethyl-2-*exo*-methoxy-4-phenyl-7-azabicyclo[2.2.1]heptane was made on the basis of spectroscopic data and by single-crystal x-ray diffraction[9] of its ammonium perchlorate derivative (mp 288–290 °C, from $CHCl_3$) (Figure 1).[10] Photolysis of **11** (4.3 mM) in 25% aqueous acetonitrile was shown to follow a similar course; workup of the crude photolysate in the manner described above followed by preparative GLC (OV-101, 170 °C) gave the *exo*-azabicycloheptanol **13** (58%, mp 96–98 °C). Structural and stereochemical assignments to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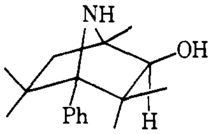
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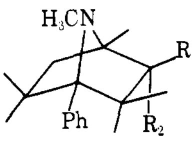
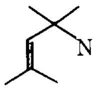

14a, R_1 = OCH_3; R_2 = H
b, R_1 = H; R_2 = OCH_3

13 were made on the basis of spectroscopic data and the conversion of this photoproduct to the *exo*-methyl ether **12** (NaH, CH_3I, THF, reflux).

Irradiation of the *N*-methylpyrrolinium perchlorate **10** in methanol (2.8 mM) using Corex-filtered light afforded after base workup and silica gel TLC (Et_2O) the 7-methyl-7-azabicycloheptyl methyl ether **14** (22%) as a 4:1 mixture of exo (**14a**) and endo (**14b**) isomers. The conversion of **12** to **14a** (dimethyl sulfate, K_2CO_3, THF, reflux) serves to confirm the structure and stereochemistries of **14a** and **14b.**

Importantly, dark control reactions conducted under a variety of conditions (e.g., refluxing aqueous or methanolic solutions of **10** and **11** for 24 h) failed to promote reaction of the isobutenyl-1-pyrrolinium salts. Direct irradiation of the neutral pyrroline **9** in methanol, acetonitrile, or *tert*-butyl alcohol leads to consumption of the starting material, but does not produce the cyclization products observed above. In each case, trace quantities of a number of products along with polymeric materials are generated. Lastly, benzophenone-sensitized irradiation of **11** in methanol results in inefficient production of **12** under conditions in which **11** is completely consumed. Thus, the photocyclization reactions of **10** and **11** are definitely photochemical in nature and appear to initiate from the singlet excited states of the pyrrolinium salts.



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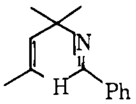

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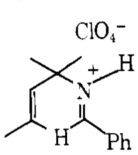

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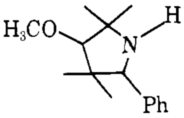
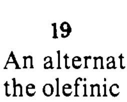


18

The generality of the photocyclization reaction has been briefly probed. The acyclic *N*-allyliminium perchlorate, **17**, prepared by condensation of the tetramethylallylamine **15** with benzaldehyde followed by treatment of the derived imine **16** with perchloric acid, undergoes smooth photocyclization in methanol to produce (51%) the methoxypyrrolidines **18** as a 4:1 isomeric mixture.[11]

Although information on the mechanistic details of this novel photocyclization reaction is minimal, tentative yet reasonable rationale can be advanced. Intramolecular [2 + 2] photocycloaddition of the olefinic π moiety to the singlet excited iminium chromophore would lead to the production of the short-lived aziridinium salt **19**.[12,13] Collapse of this bicyclic intermediate by heterolytic cleavage of the internal C–N bond followed by rapid solvent capture of the resultant carbenium ion **20** would furnish the 3-substituted pyrrolidines. An alternate pathway having nucleophilic attack on **19** in concert with C–N bond cleavage appears unlikely since the preferrence for *exo*-methoxyl and -hydroxyl stereochemistry in products from reaction of **10** and **11** would not be consistent with displacement reactions of solvent at C-7 of intermediate ammonium ions **21** having the 7-azatricyclo[$2.1.0.0^{2,7}$]heptane skeleton.[14]



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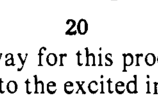

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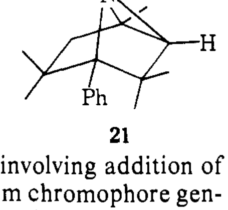

21

An alternate pathway for this process, involving addition of the olefinic moiety to the excited iminium chromophore generating **20** directly, cannot be ruled out owing to our current minimal knowledge about the chemical and physical characteristics of iminium salt excited states.

Studies to probe more deeply the mechanistic details and almost certain synthetic applications of this new excited state reaction are continuing.

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(3) R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland, and A. Todd, *J. Chem. Soc.*, 2094 (1959).

(4) Super-magnesium used to prepare isobutenyl magnesium bromide was made by the method of R. D. Rieke and S. E. Bates, *J. Am. Chem. Soc.*, **96**, 1775 (1974).

(5) Satisfactory spectroscopic and elemental analytical data were obtained for all new compounds.

(6) (a) This material was obtained as a mixture of diastereomers from which one could be obtained in pure form by recrystallization from pentane (mp 115–116 °C, 39%). (b) The diastereomeric mixture (mp 51–54 °C) consisted mainly (9:1) of one isomer.

(7) Addition of $HClO_4$ to **9** cause a simultaneous decrease in the UV maximum at 234 nm and an appearance of a new absorption at 266 nm (log ϵ 4.05) with an isosbestic point at 247 nm. Complete reversal of this change is noted upon addition of base.

(8) (a) Irradiations were conducted in a preparative apparatus consisting of a Hanovia 450-W medium-pressure lamp in a water-cooled quartz immersion well, under an Ar atmosphere. Reactions were monitored by changes in UV and GLC characteristics of removed aliquots. Typical irradiation times to obtain nearly complete conversion ranged from 40 min to 33.75 h. (b) Spectroscopic analyses of the reaction mixtures before purification indicate that the yields for the cyclization reactions are nearly quantitative. The moderate yields obtained after purification must result from losses during chromatographic separations.

(9) The compound crystallized in space group $P2_1/C$ with 4 molecules per unit cell, and cell constants a = 10.485 (4) Å, b = 12.295 (4) Å, c = 16.101 (8) Å, β = 111.82 (3)°, V = 1926 (1) $Å^3$ at 3 °C. The space group was confirmed on film. Data were collected in the 2θ range 0 to 115° on a computer-controlled diffractometer equipped with graphite monochromater, using Cu K$\bar{\alpha}$ raidiation, with θ–2θ scans. The 1974 out of 3092 data that had intensity greater than 3 σ were used in a combination of direct methods and difference Fourier techniques to locate all nonhydrogen atoms. The R value is presently ~0.14 with an apparent inversion-like dosorder in the perchlorate ion. Complete details of the crystallographic study will be published at a later date.

(10) A trace (~1%) of the endo isomer of **12** in the photoreaction mixture is suggested by GLC analysis.

(11) Assignment of stereochemistry to the major and minor isomeric photoproducts obtained from irradiation of **17** is not possible on the basis of the spectroscopic data accumulated to date.

(12) (a) Although [2 + 2] cycloaddition reactions of olefins to the C=N bond are rare, recent reports by Swenton[12b] and Koch[12c] indicate that the reaction efficiency increases when electron-withdrawing acyl groups are present on nitrogen. (b) J. S. Swenton and J. A. Hyatt, *J. Am. Chem. Soc.*, **96**, 4879. (c) R. M. Rodehorst and T. H. Koch, *ibid.*, **97**, 7298 (1975).

(13) (a) Intramolecular [2 + 2] cycloaddition reactions of analogous 1,4-dienes are known.[13b] (b) E. Block and H. W. Orf, *J. Am. Chem. Soc.*, **94**, 8438 (1972); H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *ibid.*, **94**, 5504 (1972).

(14) (a) Although participation by nitrogen in stabilizing β-cationic centers is well known in acyclic and cyclic systems,[14b] the ring strain present in the aziridinium ions **19** and **21** could be sufficient to minimize this effect. (b) R. O. Hutchins and L. Rua, *J. Org. Chem.*, **40**, 2567 (1975).

(15) Camille and Henry Dreyfus Foundation Teacher-Scholar Grantee, 1975–1980.

(16) Petroleum Research Fund Predoctoral Fellow.

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