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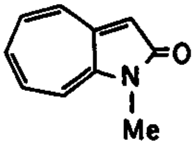
CYCLOADDITION OF 1-METHYL-1-AZAAZULEN-2(1H)-ONE WITH REACTIVE ACETYLENES

Noritaka Abe* and Toshiyuki Takehiro
Department of chemistry, Faculty of Sciences, Yamaguchi
University, Yamaguchi 753, Japan

Abstract — Reactions of 1-methyl-1-azaazulen-2(1H)-one with reactive acetylenes in refluxing acetonitrile gave 1,2-disubstituted azulene (2), 2-methylcyclopent[de]isoquinolin-3(2H)-one (3), 1-methylcyclopent[cd]azulen-2(1H)-ones (4 and 5), and 3-substituted 1-methyl-1-azaazulen-2(1H)-ones (6 and 7). When the reaction was carried out in refluxing t-butylbenzene, the compound 2 and 6,8a-etheno-1-methyl-1-azaazulen-2(1H)-one (8) were obtained as major products.

We have reported the cycloadditions of 1-azaazulenes with reactive acetylenes, which proceeded via dipolar intermediates.[1] As a continuation of our work, we advanced the reaction to 1-methyl-1-azaazulen-2(1H)-one (1) and found that 1 and reactive acetylenes underwent interesting cycloaddition reactions and rearrangement.

Treatment of 1 with dimethyl acetylenedicarboxylate (DMAD) in refluxing acetonitrile for 120 h gave dimethyl 1,2-azulenedicarboxylate (2a)[2] (9%), dimethyl 2-methyl-2,3-dihydro-3-oxocyclopent[de]isoquinoline-4,5-dicarboxylate (3a)[3] (11%), dimethyl 1-methyl-1,2,2a,3-tetrahydro-2-oxo-1-azacyclopent[cd]azulene-3,4-dicarboxylate (4a)[4] (11%), dimethyl 1-methyl-1,2-dihydro-2-oxo-1-azacyclopent[cd]zulene-3,4-dicarboxylate (5a)[5] (7%), dimethyl 1-methyl-1,2-dihydro-2-oxo-1-azaazulene-3-maleate (6a)[6] (17%), and dimethyl 1-methyl-1,2-dihydro-2-oxo-1-aza-azulene-3-fumalate (7a)[7] (21%). These structures were determined on the basis of the spectroscopic data as well as elemental analyses. Compound 3a was a stable condensed isoquinolone derivative. In its ^{1}H-nmr spectrum, a signal of 1H singlet assignable to H-1 proton is seen at δ 8.73, which is a reasonable value as 3-isoquinolone.[8] In the ^{1}H-nmr spectrum of 4a, AB doublets are seen at δ 3.10 and 4.32 (J=9.2 Hz), and in the ^{13}C-nmr spectrum, two methine signals at δ 43.14 and a: E = CO_2Me , b: E = COPh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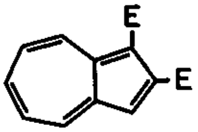
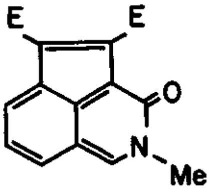
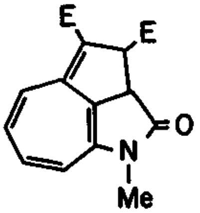
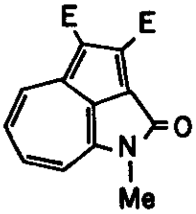
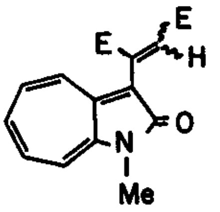

2a, b

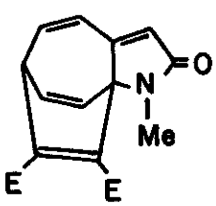

3a, b

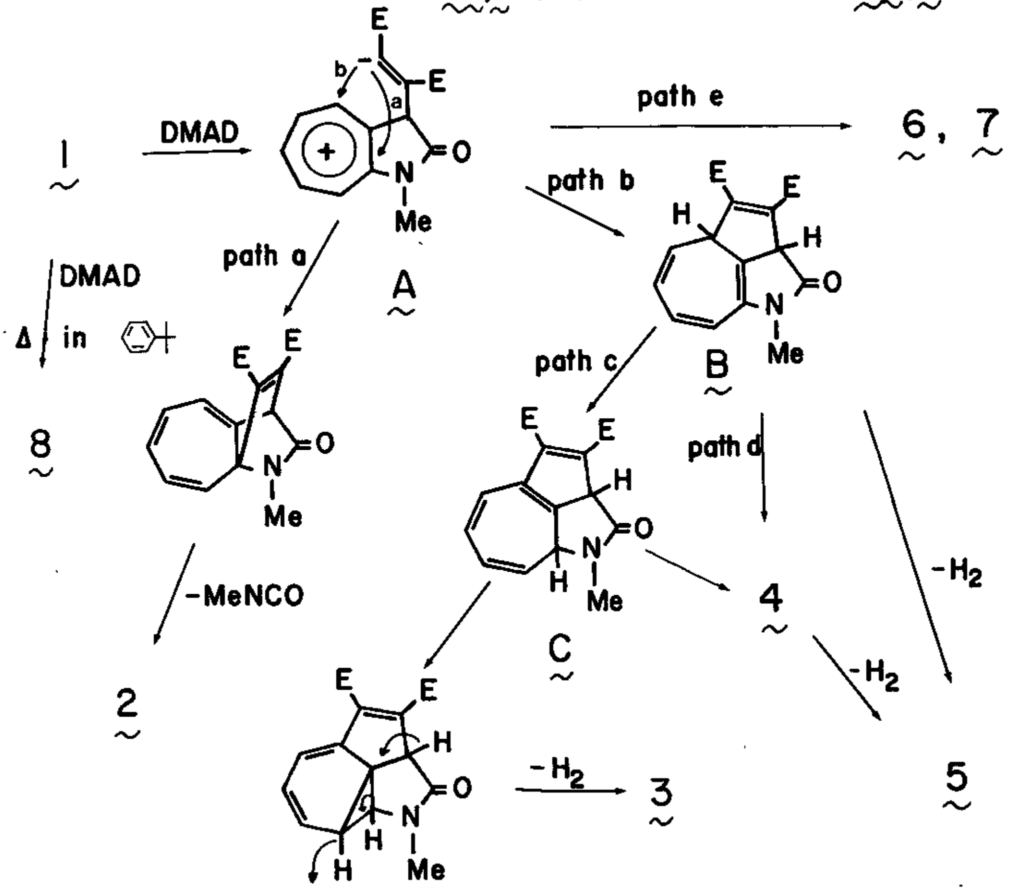

4a, b


5a, b


6a, b: (Z)-isomer

7a, b: (E)-isomer


8a, b



Scheme I

50.09. Dehydrogenation of 4a by tetrachloro-o-benzoquinone gave 5a in a 47% yield. The results associate with the structures.

When the above reaction was carried out in refluxing t-butylbenzene for 3 h, compounds 2a (21%), 3a (5%), 5a (0.8%), and dimethyl 6,8a-etheno-1-methyl-1,2-dihydro-2-oxo-1-azaazulene-7,8-dicarboxylate (8a)[9] (49%), were isolated. In the ^{13}C-nmr spectrum of 8a, signals assignable to sp^3 carbons are seen at δ 38.70 (d, C-6) and 71.55 (s, C-8a), and in its ^{1}H-nmr spectrum, methine proton is observed at δ 4.46 (ddd, J=8.5, 6.7, and 1.2 Hz, H-6). Further evidence supporting the structure of 8a is provided by its mass spectrum which displays an intense peak at m/z 159 (98%) associated with the loss of DMAD.

In a similar treatment, a reaction of 1 with dibenzoylacetylene in refluxing acetonitrile gave 2b (9%), 3b (3%), 4b (50%), 5b (6%), and 7b (6%), and in refluxing t-butylbenzene 2b (60%), 3b (19%), 5b (1.6%), and 8b (15%).[10]

A plausible mechanism is shown in Scheme 1. When DMAD attacks at C-3 position of 1, which is a reactive site towards electrophile,[11] a dipolar species A should be produced. A cyclization on C-8a position of A and a successive elimination of MeNCO furnishes 2 (path a). A cyclization on C-4 position of A gives B (path b), and a subsequent 1,5-hydrogen shift of B produces C (path c) and 4 (path d). Dehydrogenation of B and/or 4 affords 5. A tautomerization of C and a subsequent dehydrogenation lead to 3 (path c). A hydrogen shift of A gave Michael addition products 6 and 7 (path e). On the reaction in refluxing t-butylbenzene a Diels-Alder reaction occurs on seven-membered ring and 8 is obtained, in addition to the favorable cycloaddition-cycloreversion product 2. Similar periselectivity dependent on temperature is known on the reaction of 5-azaazulene with DMAD.[12]

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2. mp 53-54℃ (lit. 2a, oil; 2b, mp 45℃), MS m/z 244 (M^+, 81%), 213 (100), ^{1}H-nmr (250 MHz) δ =3.96 (s, OMe), 3.99 (s, OMe), 7.48 (t, J=9.8 Hz, H-5), 7.48 (s, H-3), 7.57 (t, J=9.8 Hz, H-7), 7.87 (t, J=9.8 Hz, H-6), 8.50 (d, J=9.8 Hz, H-4), 9.44 (d, J=9.8 Hz, H-8); 2a. W. von E. Doering and D. W. Wiely, Tetrahedron, 1960, 11, 183; 2b. I. Kawamoto, Y. Sugimura, N. Soma, and Y. Kishida, Chem. Lett., 1972, 931.

3. mp 168-169℃, MS m/z 299 (M$^+$, 100%), ^{1}H-nmr (250 MHz) δ =3.40 (s, NMe), 3.99 (s, OMe), 4.11 (s, OMe), 6.95 (dd, J=6.1 and 1.2 Hz, H-6), 7.45-7.60 (m, H-7 and 8), and 8.73 (s, H-1), ^{13}C-nmr (62.87 MHz) δ =26.36 (q), 52.84 (q), 53.08 (q), 106.85 (d), 120.59 (d), 123.86 (s), 126.08 (s), 127.81 (s), 127.99 (s), 130.21 (d), 130.50 (s), 134.04 (d), 139.85 (s), 165.30 (s), 165.38 (s), and 166.64 (s).
4. mp 151-152℃, MS m/z 301 (M$^+$, 100%), ^{1}H-nmr (250 MHz) δ =3.08 (s, NMe), 3.10 (d, J=9.2 Hz, H-2a), 3.86 (s, OMe), 3.88 (s, OMe), 4.32 (d, J=9.2 Hz, H-3), 5.66 (d, J=6.1 Hz, H-8), 6.40-6.50 (m, H-5 and 6), and 6.65-6.75 (m, H-7), ^{13}C-nmr (62.87 MHz) δ =27.14 (q), 43.14 (d), 50.09 (d), 52.33 (q), 52.55 (q), 98.33 (d), 122.19 (d), 124.69 (d), 124.75 (s), 130.83 (s), 131.29 (d), 134.43 (s), 134.68 (s), 162.86 (s), 164.40 (s), and 170.73 (s).
5. mp 190-191℃, MS m/z 299 (M$^+$, 35%), and 126 (100), ^{1}H-nmr (250 MHz) δ =3.52 (s, NMe), 3.94 (s, OMe), 4.05 (s, OMe), 7.48 (d, J=9.8 Hz, H-8), 7.72 (t, J=9.8 Hz, H-6), 8.15 (t, J=9.8 Hz, H-7), and 9.16 (d, J=9.8 Hz, H-5), ^{13}C-nmr (62.87 MHz) δ =26.55 (q), 51.67 (q), 52.72 (q), 113.74 (d), 114.03 (s), 115.22 (s), 128.29 (d), 135.17 (s), 137.11 (s), 138.93 (s), 140.87 (d), 141.40 (d), 149.96 (s), 162.79 (s), 164.23 (s), and 180.28 (s).
6. mp 123.5-124℃, ^{1}H-nmr (250 MHz) δ =3.58 (s, NMe), 3.79 (s, OMe), 3.96 (s, OMe), 7.00 (s, H-vinyl), 7.05-7.40 (m, H-5, 6, 7, and 8), 7.76 (d, J=11.0 Hz, H-4).
7. mp 150-151℃, ^{1}H-nmr (250 MHz) δ =3.58 (s, NMe), 3.68 (s, OMe), 3.81 (s, OMe), 6.90-7.30 (m, H-4, 5, 6, 7, and 8), and 7.15 (s, H-vinyl).
8. H. Fukumi and H. Kurihara, Heterocycles, 1978, **9**, 1197.
9. mp 156-158℃, MS m/z 301 (M$^+$, 100%), and 159 (98), ^{1}H-nmr (250 MHz) δ =3.05 (s, NMe), 3.77 (s, OMe), 3.78 (s, OMe), 4.46 (ddd, J=8.5, 6.7, and 1.2 Hz, H-6), 5.95 (s, H-3), 6.06 (d, J=10.4 Hz, H-4), 6.21 (dd, J=7.9 and 1.2 Hz, H-9), 6.41 (dd, J=10.4 and 8.5 Hz, H-5), and 6.66 (dd, J=7.9 and 6.7 Hz, H-10), ^{13}C-nmr (62.87 MHz) δ =26.47 (q), 38.70 (d), 52.64 (q, x 2), 71.55 (s), 120.57 (d), 121.16 (d), 129.47 (d), 132.62 (d), 133.26 (d), 134.23 (s), 145.64 (s), 147.03 (s), 163.07 (s), 164.95 (s), and 171.28 (s).
10. The spectral data of the products other than recorded in this text showed pertinent figures, and the full data will be reported elsewhere.
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12. K. Hafner and J. Haring, Erdoel Kohle, Erdgas, Petrochem., 1979, **32**, 136.

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