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A NOVEL COUPLING REACTION OF 1-AZULYLMETHYLTRIMETHYLAMMONIUM IODIDE. SYNTHESIS OF 1,2-BIS(1-AZULYL)ETHANE AND [2.2.2.2](1,3)AZULENOPHANE

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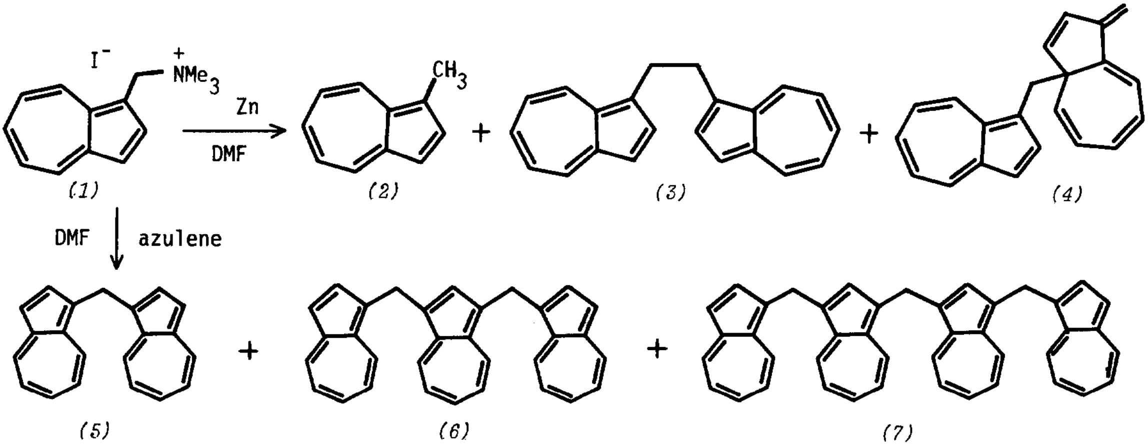
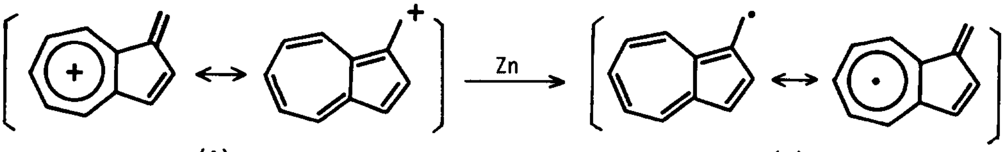
It is well known that bimolecular reduction is brought about by the action of zinc dust on an aqueous solution of tropylium ions.2) Since this reduction proceeds by a one electron transfer to give the tropyl radical as an intermediate, it may be concluded that this radical is not stable in comparison with its dimer (ditropyl) at room temperature. In an attempt to extend this reaction to the masked tropylium systems we have studied the reaction of 1-azulylmethyltrimethylammonium iodide (*1*)3) with zinc.

Treatment of the ammonium salt (*1*) [16.3 g] with a large excess of zinc powder [16.5 g] in dry DMF [300 mL] at 50°C for 20 h there was obtained in addition to the known 1-methylazulene (*2*)4) [4.4%] two new compounds (*3*) and (*4*) in 56.6% and 4.1% yield, respectively. As would be expected, the major product (*3*), blue prisms, mp 140.5-141°C, was identified as 1,2-bis(1-azulyl)ethane based on its analysis and ^{1}H-NMR spectrum [δ 3.53 (4H, s), 7.35 and 7.82 (AB-q, J=4.0 Hz), 8.15-8.40 (4H, m), 6.8-7.6 (6H, m)]. The compound (*4*), blue oil, is very sensitive to air and heat. The structure of *4* was proved as follows : i) molecular weight determination (M^+, m/e 282.1433; $C_{22}H_{18}$ requires 282.1409) indicates that it is believed to be a dimer of azulylmethyl unit. ii) infrared absorption at 867 and 881 cm^{-1} (in CCl_4) reveals the presence of an exo-methylene group which was also confirmed by two singlets at δ 4.76 and 5.14 in its NMR spectrum. iii) the relative ratio of the aromatic protons and the olefinic protons in its NMR spectrum is found to be 1 : 1 and the pattern of the aromatic region is closely similar to that of *2* and *3* indicating that one of the azulylmethyl nucleus is remained intact. iv) the methylene proton signals appeared at δ 3.07 and 3.12 as an AB-quartet (J=14 Hz) suggesting that an 1-azulylmethyl moiety is linked to either of two angular carbon atoms of the second azulene skeleton. These spectral data are consistent with the structure of *4* being that shown, expect that they do not establish whether an an 1-azulylmethyl group resides at C-3a or C-8a.

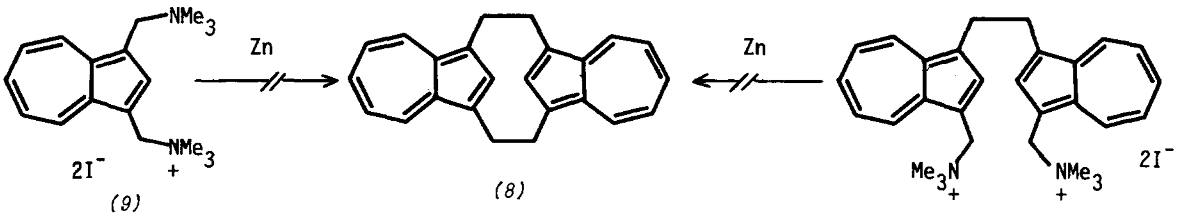
The formation of these products can be best rationalized in terms of the resonance stabilized cation intermediate (A)5) which then undergo one-electron reduction to the stable radical (B). A clear indication of the intervention of (A) was obtained in the reaction of *1* with azulene in the absence of zinc. Thus, when a solution of *1* and 1.8 mole equivalents of azulene in DMF was heated at 85-90°C for 3 h, three products were isolated in good over-all yield. The major product [40-50%], blue needles, mp 81-82°C, proved to be bis(1-azulyl)methane (*5*)3b, 5) on the basis of its elemental analysis, mass [M^+, m/e 268] and NMR spectrum [δ 4.85 (s, 2H), 8.26, 8.40 (d, J=9 Hz, 2H each), 6.83-7.75 (m, 10H)]. The second product [34%], greenish blue needles, mp 138.5-140°C, and the third product [5%], greenish blue needles, mp 137.5-138.5°C, were the trimer (*6*)6) and the tetramer (*7*)7, 8) respectively, as indicated by their analyses, mass, and NMR spectra.





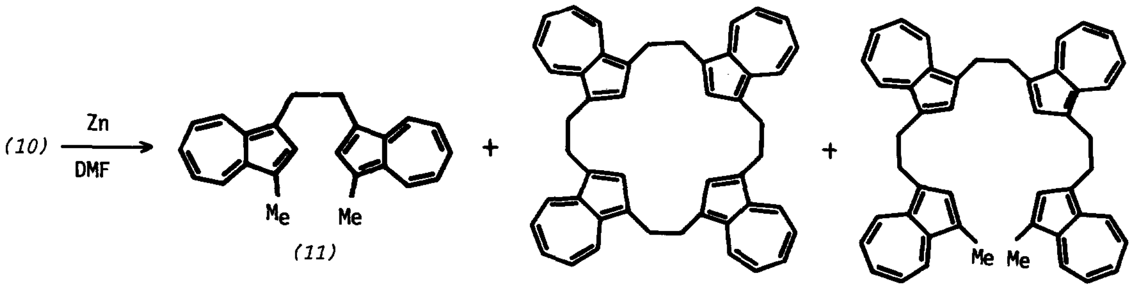
The foregoing coupling reaction of *1* provides a possibility of a new synthetic approach to the [2.2](1,3)azulenophane (*8*) from azulyl-1,3-bis(trimethylammonium) diiodide (*9*)3) readily available from azulene. Unfortunately, attempts to convert the bis-ammonium salt (*9*) to the unknown cyclophane (*8*) have so far been unsuccessful. Since intramolecular cyclization is probably more commonly carried out, we chose to use the 1,1'-bis(trimethylammonium) salt (*10*) as a starting material.

Mannich reaction of *3* with formaldehyde and tetramethyldiaminomethane affords 3,3-bis-(dimethylaminomethyl) derivative, blue prisms, mp 104-105°C, which gives the bis-methiodide (*10*) when treated with methyl iodide in the usual way.



(9) *(8)* *(10)*

Treatment of *10* with zinc dust in DMF under a high dilution condition resulted in the formation of a large amount of polymeric products. However, we isolated, by liquid chromatographic work-up[9)] of a benzene soluble portion of the reaction mixture, three products together with a minute amount of an unidentified product. The first product, mp 108.5-109°C, formed in 7% yield as blue needles from hexane-benzene, was proved to be 1,1'-dimethyl-3,3'-biazulylethane (*11*) on the basis of its analysis, and NMR spectrum [δ 2.62 (s, 6H, $-CH_3$), 3.43 (s, 4H, $-CH_2-CH_2-$), 7.64 (s, 2H), 8.1 (m, 4H) and 6.7-7.7 (m, 6H)]. The second product, greenish blue needles, mp 247°C (decomp.) [0.1%] was [2.2.2.2](1,3)azulenophane (*12*) as indicated by its symmetrical NMR pattern [δ 3.11 (s, 16H), 6.47 (s, 4H), 7.78 (d, 8H, J=10 Hz), 7.24 (t, 4H, J=10 Hz) and 6.70 (t, 8H, J=10 Hz)], and mass spectrum (M^+, m/e 616.3134; $C_{48}H_{40}$ requires 616.3130). Unusually high field chemical shift of the protons attached to 2-positions of the azulene nuclei is consistent with the cyclic structure. The third product, greenish blue needles, mp 151-152°C [∿1%], was assigned the linear tetramer structure (*13*) on the basis of its mass spectrum (M^+, m/e 618.3318; $C_{48}H_{42}$ requires 618.3286), and NMR spectrum [a singlet of two equivalent methyl groups at δ 2.64 (6H) and two singlets assigned to the ethylene protons at 3.40 and 3.44 along with aromatic protons signals at 8.05-8.21 (8H), 7.43 and 7.45 (each 2H, t, J=10 Hz), 7.60 and 7.64 (each 2H, s), 6.86 (t, 2H, J=10 Hz), 6.93 (t, 6H, J=10 Hz)].



(11) *(12)* *(13)*

As described above, the expected cyclic dimer, viz. [2.2](1,3)azulenophane (*8*) could not be detected in the reaction mixture.10) The failure to produce the desired azulenophane is believed to partly be due to the unfavorable dipole-dipole interaction between two azulene nuclei exist in the transition state of the intramolecular coupling reaction.

REFERENCES AND FOOTNOTES

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3) (a) M. Muhlstadt, W. Treibs, and J. Mohr, *Chem. Ber.*, 94, 808 (1961); A. G. Anderson, Jr., R. G. Anderson, and T. S. Fujita, *J. Org. Chem.*, 27, 4535 (1962); A. G. Anderson, Jr., and R. D. Breazeale, *ibid.*, 34, 2375 (1969).
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4) Cf. W. Keller-Schierlein and E. Heilbronner, "Nonbenzenoid Aromatic Compounds" D. Ginsburg Ed., Interscience, New York, p. 277 (1959).

5) K. Hafner and his co-workers reported that several stable 1-alkylideneazulenium ions were formed from α-dialkylaminoalkylazulenes or α-hydroxyalkylazulenes and that chloromethylation and hydroxymethylation of azulene gave bis(1-azulyl)methane (*5*). K. Hafner, H. Pelster, and J. Schneider, *Liebigs Ann. Chem.*, 650, 62 (1961).

6) Compound *6* : mass spectrum [M^+, m/e 408], NMR spectrum [δ 4.78 (s, 4H), 6.72-7.73 (m, 14H), 8.06-8.50 (m, 6H)].

7) Compound *7* : NMR Spectrum [δ 4.75 (s, 2H), 4.78 (s, 4H), 6.80-7.26 (m, 6H), 7.30-7.62 (m, 6H), 8.24-8.46 (m, 8H)].

8) W. Treibs, M. Muhlstadt, and K.-D. Kohler, *Naturwissenschaften*, 45, 336 (1958).

9) The isolation of *11*, *12*, and *13* by use of a Liquid Chromatograph (LC-8, Nihon Bunko Kogyo K. K., column:JAIGEL-2; solvent:chloroform) was carried out through the kind courtesy of Professor S. Misumi (Osaka University). The authors wish to express their gratitude to him for this help.

10) Quite recently, [2.2](1,3)azulenophane (*8*) has been synthesized by Professor S. Itô and his co-workers. Cf. Abstracts of Papers, 11th Symposium on Nonbenzenoid Aromatic Compounds, p. 181, October 6-7, 1978, Osaka.

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