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Synthesis of Methyl Azulen[1,2-*b*]azulene-2-carboxylate and Dimethyl Azulen[1,2-*b*]azulene-2,4-dicarboxylate

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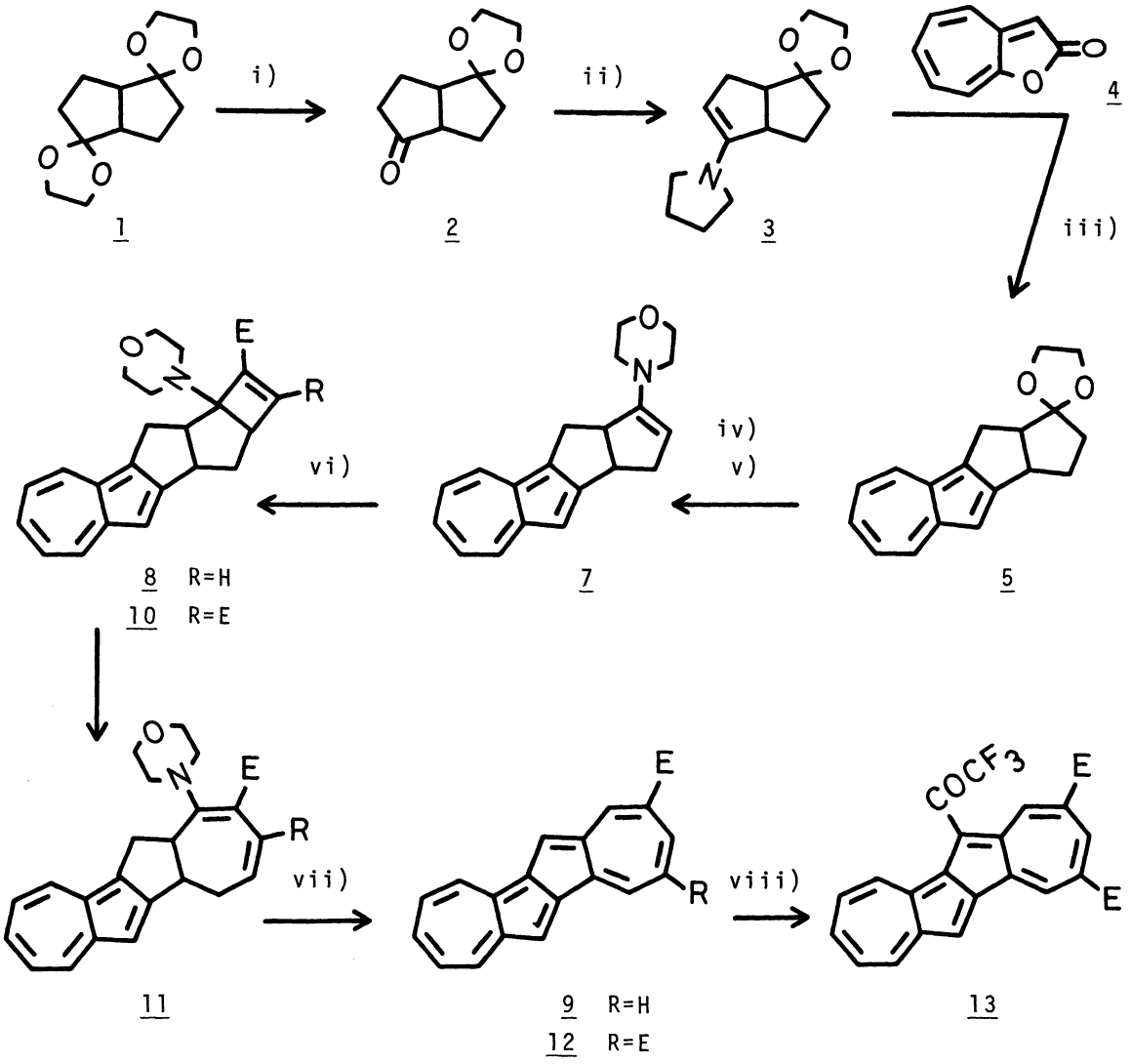
The titled compounds were synthesized. The complete assignment of ^{1}H-NMR spectrum of methyl azulen[1,2-*b*]azulene-2-carboxylate and the rearrangement of ester group on seven membered ring in the dehydrogenation reaction are described.

In the last decade, three isomers of the cata condensed nonalternant hydrocarbon of azulenazulenes[1] have been synthesized by C. Jutz,[2] T. Toda,[3] and Z. Yoshida.[4] However, the type of azulen[1,2-*b*]azulene is so far isolated as a 6,12-diaryl substituted derivative in which the ^{1}H-chemical shifts of five membered ring protons and two types of seven membered ring protons are inherently hidden by the substituents. Here we wish to report the synthesis of simpler titled compounds and the complete assignment of ^{1}H-NMR spectrum of mono-substituted azulen[1,2-*b*]azulene 9 by the two dimentional and NOE measurements. Further the rearrangement of ester group on seven membered ring in the dehydrogenation reaction was observed.

The synthetic procedure was based upon azulene synthesis by the reaction of 2H-cyclohepta[*b*]furan-2-one 4 with enamine[5] and by the ring expansion of the adduct of acetylene derivative with enamine.[6] The reaction of mono-ketal of bicyclo[3.3.0]cyclooctan-3,8-dione 2 and morpholine in the presence of a large amount of anhydr. $MgSO_4$ in dry ether at reflux for 3 h furnished the enamine 3 as a pale yellow oil in 78% yield. The reaction of 3 with 4 in refluxing toluene for 3 h gave an azulene 5 as blue needles in 35% yield. The hydrolysis of 5 with dil. HCl in acetone at r.t. for 3 h gave a ketone 6 in over 90% yield. The reaction of 6 with morpholine in benzene in the presence of titanium tetrachloride at r.t. for 5 h furnished an enemine 7 as a moisture sensitive blue oil, which was immediately treated with methyl propiolate in dry toluene at reflux for 3 h to give adduct 8 as blue needles in 48% yield. After many attempts, dehydrogenation of 8 was achieved by using Pd-C in diphenyl ether at reflux for 7-9 min to give a fully dehydrogenated 9 accompanied by the loss of morpholine molecule on 1-position as reddish purple needles in 3% yield. The complete assignment of ^{1}H-NMR spectrum of 9 was obtained by the method of ^{1}H-^{1}H two dimentional (the correlation of neigh-



i) H_3O^+/THF/r.t./3 h. ii) morpholine/anhydr. $MgSO_4$/ether, reflux/3.5 h. iii) toluene, reflux/8 h., and then SiO_2/95-100 °C/1 h. iv) H_3O^+/acetone/r.t./3 h. v) $TiCl_4$/morpholine/benzene/r.t./5.5 h. vi) HC≡C-COOMe or DMAD/toluene, reflux/3 h. vii) Pd-C/diphenyl ether, reflux/7-9min. viii) $(CF_3CO)_2O/CH_2Cl_2$/r.t./30 min.

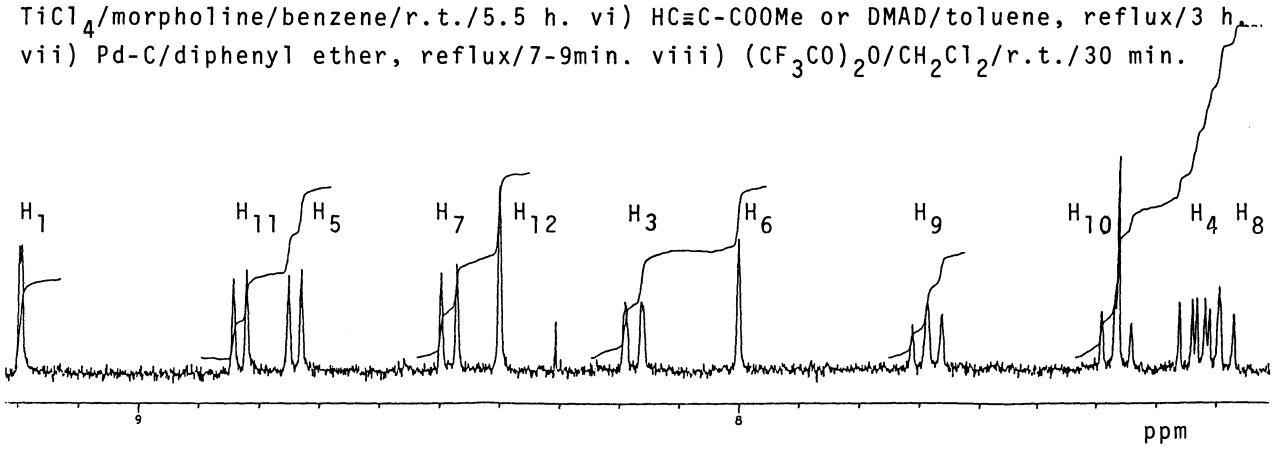


Fig. 1. The 400 MHz ^{1}H-NMR spectrum of 9 in DMSO-d_6.

boring protons on seven membered ring was clarified) and NOE (H_6 with H_7 and H_1 with H_{12}) measurements as shown in the table and figure. It is noted that the assignment of H_8 and H_{11} of 9 is reversed to those of corresponding diaryl substituted derivative.[3] Then the reaction of 7 with dimethyl acetylenedicarboxylate (DMAD) in dry toluene under the similar conditions as above gave an adduct 10 as blue needles and ring opened 11 as blue needles in 26% and 19% yield, respectively. Heating of 10 in refluxing xylene for 12 h furnished 11 in over 90% yield. The dehydrogenation of 11 under the similar conditions as above gave a fully dehydrogenated and unexpectedly ester group migrated 12 as purple needles in 8% yield. The structure of 12 was confirmed by the spectral data especially by the ^{1}H-NMR spectrum. The protons on 1-, 3-, and 5-positions were determined by their meta coupling of H_1 with H_3 and H_3 with H_5, and the assignments of the other protons (H_{6-12}) were based upon the comparison with those of 9. The formal migration of ester group from 3- to 4-position is a new type of rearrangement.[7] Although the average of chemical shifts of unsubstituted azulene moiety of 9 and 12 which may be more suitable for comparison are slightly shifted to lower field than those of azulen[1,2-*f*]-, azulen[1,2-*b*]-, and azulen[2,1-*e*]-azulenes,[2-4] and the differences of the coupling constants of seven memebred ring protons of 9 and 12 are smaller than those of above azulenazulenes, the compounds of 9 and 12 are mainly composed of two azulene moieties. The UV spectra of 9 and 12 showed the absorption maximum at the long wave-length region around 1200 nm and the other absorption maxima also very much similar to those of diaryl substituted derivative[3] in accordance with calculated one.[2,3]

An electrophilic substitution reaction of 12 with trifluoroacetic anhydride occured unexpectedly on 12-position of 12 exclusively despite of it placed on less reactive azulene moiety due to the substituted ester groups. The structure of 13, obtained in 90% yield from 12, was confirmed by the ^{1}H-NMR spectrum, since the chemical shift of H_1 was observed at the lowest field by the anisotropic effect of trifluoroacetyl group on 12-position. Since there was not isolated the other mono or ditrifluoroacetylated compound, it is suggested that the introduced trifluoroacetyl group deactivate the both azulene moieties.

Table 1. Physical properties of new compounds

7: blue oil; IR (film) 1720, 1700, 1630 cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 7.88(m,2H), 7.05(m,4H), 4.17(m,1H), 4.01(m,1H), 3.65(m,4H), 3.22(m,3H), 2.75(m,6H); MS m/e 291 (M^+, 100%): Calcd for $C_{20}H_{21}NO$: 291.1623, measured: 291.1628.

8: blue needles, mp 165-167 °C; IR (KBr) 1708, 1612, 1267 cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 8.10(d,J=9.3 Hz,1H), 8.04(d,J=9.1 Hz,1H), 7.33(t,J=9.7 Hz,1H), 7.24-6.81 (m,4H), 3.84-3.68(m,8H), 3.50-3.17(m,4H), 2.81(dd,J=4.6, 4.4 Hz,1H), 1.97-1.50(m, 2H); MS m/e 375 (M^+, 100%); Calcd for $C_{24}H_{25}NO_3$: 375.1832, measured: 375.1817.

9: reddish purple needles, mp 212-213 °C(dec. without melt); IR (KBr) 1699, 1579, 1223 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 9.19(d,J=1.60 Hz,H_1), 8.83(d,J=8.85 Hz, H_{11}), 8.74(d,J=8.54 Hz,H_5), 8.48(d,J=10.00 Hz,H_7), 8.40(s,H_{12}), 8.17(dd,J=1.60, 11.60 Hz,H_3), 8.00(s,H_6), 7.69(dd,J=9.76, 10.07 Hz,H_9), 7.37(dd,J=8.85, 10.07 Hz,

H_{10}), 7.23(dd,J=8.54, 11.60 Hz,H_4), 7.20(dd,J=9.76, 10.00 Hz,H_8), 3.93(s,3H,OMe); MS m/e 286 (M^+, 100%); Calcd for $C_{20}H_{14}O_2$: 286.0992, measured: 286.0982; UV λ_{max} (CH_2Cl_2) 1200(logε=2.35), 1110(2.48), 507(4.02), 480(3.91), 360(4.87), 255 nm (4.13).

11: blue needles, mp 183 °C; IR (KBr) 1700, 1665, 1250 cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 8.16(d,J=9.0 Hz,1H), 7.95(d,J=9.5 Hz,1H), 7.50(dd,J=9.7, 9.6 Hz,1H), 7.11 (s,1H), 7.06(dd,J=9.7, 9.6 Hz,1H), 7.05(dd,J=9.7, 9.5 Hz,1H), 6.25(t,J=7.5 Hz,1H), 4.49(m,1H), 3.97(m,1H), 3.90-3.51(m,6H), 3.61(s,3H,OMe), 3.56(s,3H,OMe), 3.17(m, 4H), 2.59(m,2H); MS m/e 433 (M^+, 100%).

12: reddish purple needles, mp 221 °C(dec.); IR (KBr) 1700, 1250 cm^{-1}; ^{1}H-NMR (200 MHz, DMSO-d_6) δ 9.29(d,J=1.4 Hz,H_1), 9.24(d,J=1.9 Hz,H_5), 9.16(dd,J=1.9, 1.4 Hz, H_3), 8.89(d,J=8.3 Hz,H_{11}), 8.62(s,H_{12}), 8.52(d,J=10.0 Hz,H_7), 8.07(s,H_6), 7.74(t, J=10.3 Hz,H_9), 7.45(dd,J=8.3, 10.3 Hz,H_{10}), 7.30(dd,J=10.3, 10.0 Hz,H_8), 3.96(s, 3H,OMe), 3.95(s,3H,OMe); MS m/e 344 (M^+, 100%); Calcd for $C_{22}H_{16}O_4$: 344.1005, measured: 344.1004; UV λ_{max} (CH_2Cl_2) 1200(logε=2.20), 541(4.11), 508(4.02), 370 nm (4.79).

13: deep purple needles, mp 282-284 °C; IR (KBr) 1717, 1710, 1630, 1230, 740 cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 10.33(s,H_1), 9.36(s,H_3, H_5), 9.16(d,J=10.5 Hz,H_{11}), 9.05 (d,J=9.0 Hz,H_7), 8.23(s,H_6), 8.02-7.74(m,H_8, H_9, H_{10}), 4.07(s,3H,OMe), 4.03(s,3H, OMe); MS m/e 440 (M^+, 100%), 343(42); Calcd for $C_{24}H_{15}O_5F_3$: 440.0869, measured: 440.0836.

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7) The similar rearrangement of ester group also occured in a simpler system of these compounds. The result will be submitted for the publication elsewhere.

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