Preparation of Tetraphenylazulenequinodimethanes from the Reactions of Azulenequinones with Diphenylketene and the ^{1}H NMR and UV-vis Spectral Studies in Acidic Media

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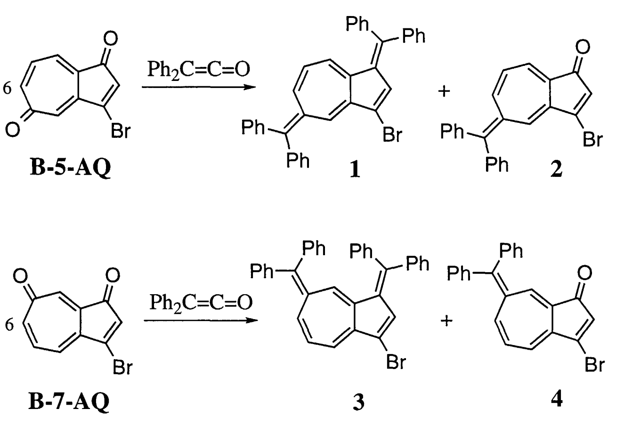
3-Bromo-1,5-azulenequinone and 3-bromo-1,7-azulenequinone reacted with diphenylketene to give the corresponding tetraphenylazulenequinodimethane, which has both diphenylfulvene and diphenylheptafulvene structures. The protonation occurred at the diphenylmethylene group on the seven-membered ring to form a cycloheptatrienylium ion.

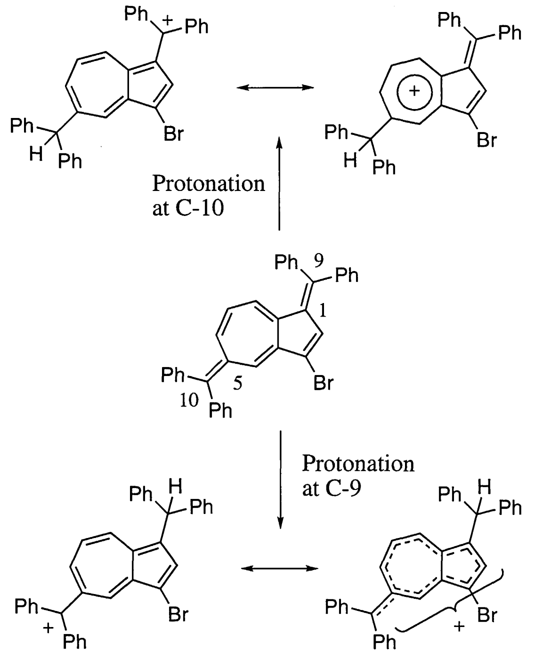
Much attention has been paid for the synthesis and properties of a new class of π-conjugated systems. We designed a novel extended π-system with an azulenequinodimethane structures from the reaction of azulenequinones and ketenes since ketenes react with ketones to introduce methylene groups after elimination of carbon dioxide from the adduct. In troponoids, however, it is known that 4,5-benzotropone[1] and 2-methoxytropone[2] react with diphenylketene to give corresponding diphenylheptafulvene derivatives whereas tropone[3] gives an [8+2] adduct. Here, we show the synthesis of tetraphenylazulenequinodimethanes and the ^{1}H NMR and UV-vis spectral studies in acidic media.

A toluene solution of **B-5-AQ** and diphenylketene, generated *in situ* from the thermolysis of the diazonium salt prepared by the oxidation of benzil monohydrazone with mercury oxide, was heated to give two products (**1** and **2**) in 39 and 21% yields, respectively. From the spectral data,[4] the structure of the main product **1** was determined to be 3-bromo-9,9,10,10-tetraphenylazulenequino-1,5-dimethane, which has both diphenylfulvene and diphenylheptafulvene moieties. The minor product **2** has an absorption band of a cyclopentenone group at 1692 cm^{-1} in the IR spectrum and a carbonyl carbon signal at δ 189.3 in the ^{13}C NMR spectrum, which indicated that **2** was 3-bromo-9,9-diphenylazulenequino-5-methide.[5] Similarly, the reaction of **B-7-AQ** and diphenylketene afforded 3-bromo-9,9,10,10-tetraphenylazulenequino-1,7-dimethane (**3**) and 3-bromo-9,9-diphenylazulenequino-7-methide (**4**) in 37 and 13% yields, respectively.



Scheme 1.

When the ^{1}H NMR spectrum of **1** was measured in a mixture of trifluoroacetic acid (1.5%) and chloroform-*d*, the olefinic protons shifted at the lower field and a singlet signal appeared at δ 6.10, which is close to the chemical shifts (6.07-6.14) of the methine protons of (1-azulenyl)diphenylmethane (**5**). The ^{13}C NMR spectrum in a mixture of trifluoroacetic acid (1.5%) and chloroform-*d* showed the carbon signal at δ 174.2, which is close to the chemical shifts (168.6-177.7) of the methine carbons of (1-azulenyl)diphenylmethyl cation (**6**).[6] These results supported that the protonation occurred at a diphenylmethylene group to form an azulenyldiphenylmethyl cation. It has been reported that the methyl carbon of triphenylmethyl cation in chlorosulfonic acid appeared at δ 211.9.[7] As the chemical shifts of the exocyclic methylene carbons of **1** are around δ 140 in chloroform-*d*, the observed value (δ 174.2) in a mixture of trifluoroacetic acid (1.5%) and chloroform-*d* was roughly close to the average value of the chemical shifts of the exocyclic methylene and the carbonium carbons.



Scheme 2.

The trifluoroacetic acid titrations of **1** were monitored by absorption spectroscopy as illustrated in Figure 1. A distinct red-

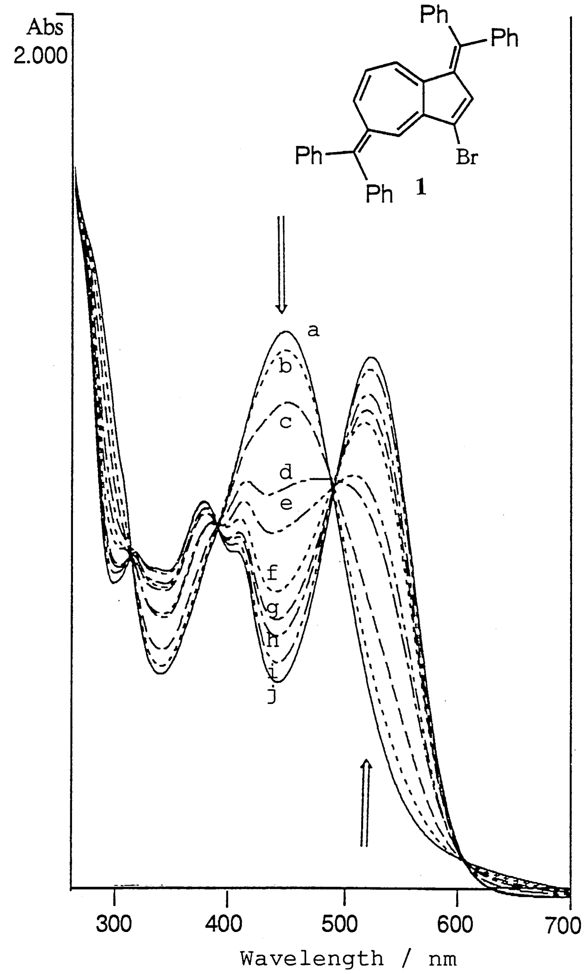
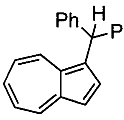


Figure 1. UV-vis spectral changes of **1** at various volume percentages of CF_3COOH in $CHCl_3$; a: 0%, b: 0.003%, c: 0.004%, d: 0.006%, e: 0.007%, f: 0.008%, g: 0.009%, h: 0.010%, i: 0.012%, and j: 0.014%.



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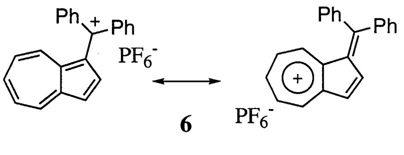

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shift was observed with showing clear isosbestic points, which supported a two-stable equilibrium. The absorption band at 527 nm was assigned to the cycloheptatrienylium ion[8] from the consideration of the substituent effect of a bromine atom at C-3 and an alkyl substituent at C-5 since **6** had an absorption at 487 nm in acetonitrile.[6] The UV-vis and NMR spectra of **3** from **B-7-AQ** behaved similarly.

It is interesting to note that the protonation occurred preferentially at the diphenylmethylene group at C-9 of the seven-membered ring. Certainly, the generation of the cycloheptatrienylium ion determined the site of the protonation.

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References and Notes

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4 New compounds have been fully characterized: **1**; Reddish crystals, mp 210-211 °C; Anal. Found: C, 80.22; H, 4.89%. Calcd for $C_{36}H_{25}Br$: C, 80.44; H, 4.69%. ^1H NMR ($CDCl_3$) δ 5.24 (1H, dd, J=12.5, 8.1 Hz), 5.57 (1H, d, J=8.1 Hz), 6.32 (1H, dd, J=12.5, 2.6 Hz), 6.70 (1H, d, J=2.6 Hz), 6.79 (1H, s), and 7.14-7.32 (20H, m); ^{13}C NMR ($CDCl_3$) δ 125.1, 127.0, 127.1, 127.2, 127.5, 127.6, 127.9, 128.2 (2C), 128.4 (2C), 128.5 (2C), 128.7 (2C), 129.2, 129.7 (2C), 129.8 (2C), 130.1 (2C), 130.2 (2C), 134.2, 136.3, 136.4 (2C), 137.0, 138.9, 139.0, 140.0, 141.9, 142.2, 142.3, and 142.9; UV (CH_3OH) λ 235.3 nm (ε 7650, sh), 272.4 (6750), and 438.8 (6960).
2; Reddish crystals, mp 166-167 °C; Anal. Found: C, 71.69; H, 4.08%. Calcd for $C_{23}H_{15}OBr$: C, 71.33; H, 3.90%. ^1H NMR ($CDCl_3$) δ 5.77 (1H, dd, J=12.1, 7.3 Hz), 6.62 (1H, d, J=0.7 Hz), 6.67 (1H, dd, J=12.1, 2.2 Hz), 6.68 (1H, d, J=7.3 Hz), 6.98 (1H, d, J=2.2 Hz), and 7.17-7.37 (10H, m); ^{13}C NMR ($CDCl_3$) δ 124.0, 128.3, 128.4, 128.5 (3C), 128.6 (3C), 129.0, 130.0 (2C), 130.1 (2C), 133.1, 133.9, 134.4, 134.6, 141.0, 141.4, 149.5, 149.8, and 189.3; UV (CH_3OH) λ 234.0 nm (ε 16100, sh), 270.5 (15210), 301.8 (11670, sh), and 446.2 (16100).
3; Reddish crystals, mp 188-190 °C; Anal. Found: C, 80.44; H, 4.93%. Calcd for $C_{36}H_{25}Br$: C, 80.44; H, 4.69%. ^1H NMR ($CDCl_3$) δ 5.75 (1H, dd, J=12.1, 7.7 Hz), 6.05 (1H, dd, J=7.7, 0.7 Hz), 6.26 (1H, dd, J=12.1, 2.2 Hz), 6.53 (1H, d, J=2.2 Hz), 6.66 (2H, m), 6.82 (1H, s), and 7.01-7.28 (18H, m); ^{13}C NMR ($CDCl_3$) δ 122.7, 125.3, 125.5, 126.5, 127.0, 127.1, 127.6, 127.9, 128.0 (4C), 128.4 (3C), 128.6, 128.8, 129.1, 129.8, 130.1, 130.2, 130.5 (3C), 134.3, 134.7, 135.2, 136.2, 137.7, 138.0, 139.8, 141.5, 141.7, 142.8, 143.2, and 144.5; UV (CH_3OH) λ 234.6 nm (ε 15550, sh), 304.7 (12820), and 445.5 (5730).
4; Reddish crystals, mp 156-157 °C; Anal. Found: C, 71.53; H, 4.10%. Calcd for $C_{23}H_{15}OBr$: C, 71.33; H, 3.90%. ^1H NMR ($CDCl_3$) δ 5.79 (1H, dd, J=12.5, 7.7 Hz), 6.30 (1H, d, J=7.7 Hz), 6.54 (1H, dd, J=12.5, 2.2 Hz), 6.64 (1H, s), 7.14 (1H, d, J=2.2 Hz), and 7.15-7.35 (10H, m); ^{13}C NMR ($CDCl_3$) δ 124.2, 127.4, 128.3, 128.5 (2C), 128.6 (2C), 128.7, 130.0 (2C), 130.1 (2C), 130.6, 133.1, 133.7, 134.7, 137.8, 139.1, 141.1, 141.7, 147.7, 151.4, and 189.3; UV (CH_3OH) λ 234.6 nm (ε 17050, sh), 272.4 (16800), 296.1 (11420, sh), and 441.7 (13240).

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8 Heat of formation of the cycloheptatrienylium ion protonated at C-10 of **1** was calculated to be 358.53 kcal/mol by MNDO/PM3 with MOPAC version 6 program which is more favorable than the value (373.54 kcal/mol) of the species protonated at C-9.