(TLC control), the reaction mixture is acidified with 3 N HCl. Then the catalyst is filtered off and the solvent is removed in vacuo. The residue was used without further purification, assuming that the reduction had occurred quantitatively.

4-Diazo-3,5-dimethyl-2,5-cyclohexadienone (5e). A 174-mg (1-mmol) portion of 4-amino-3,5-dimethylphenol hydrochloride is dissolved in 4 mL of dilute sulfuric acid (0.05 mL H_2SO_4/4 mL H_2O). Now a solution of 0.11 g (1.6 mmol) of sodium nitrite in 4 mL of H_2O is added slowly; the temperature should not exceed 5 °C. After stirring the solution at 20 °C for 20 min; 10 mL of benzene and 2.8 g of barium carbonate are added. Separation of the organic layer and evaporation of the solvent at 20 °C yields a residue which is purified over a silica column: Eluation with CH_2Cl_2/20% pentane first yields 2,6-dimethyl-1,4-benzoquinone.

Subsequent elution with CH_2Cl_2/20% CH_3OH then yields 90 mg (61%) of **5e** as orange crystals. Mp: 124 °C. Precision mass calcd 148.0636, found 148.0636 ± 2 ppm. ^{1}H-NMR ($CDCl_3$): δ 2.24 (s), 6.21 (s). ^{13}C-NMR (CD_3COCD_3): δ 18.0, 77.8, 125.6, 140.6, 181.8. MS: *m/e* 149 (9), 148 (molecular peak; 26), 120 (42), 107 (46), 93 (6), 92 (34), 91 (100), 79 (10), 77 (35), 74 (5), 66 (5), 65 (20), 63 (11), 61 (6), 53 (9), 52 (20), 51 (29), 50 (17), 45 (9), 44 (40). IR (Ar, 10 K): 2090.5 (w), 2070.7 (vs), 2067.3 (s), 2062.0 (m), 2059.1 (m), 2052.4 (m), 1634.4 (vs), 1618.5 (w), 1607.9 (vw), 1599.7 (vw), 1596.3 (vw), 1464.2 (vw), 1434.8 (vw), 1359.6 (vw), 1354.3 (w), 1350.4 (m), 1284.4 (vw), 1280.5 (vw), 1239.0 (m), 907.3 (vw), 904.0 (vw), 875.0 (vw), 708.2 cm^{-1} (vw).

4-Diazobenzo-2,5-cyclohexadienone (5f). Diazo ketone **5f** was prepared from 4-amino-1-naphthol hydrochloride according to a literature procedure.[20] IR (Ar, 10 K): 2071.7 (vs), 2051.4 (w), 1645.9 (s), 1643.5 (s), 1636.8 (m), 1624.3 (vw), 1610.3 (w), 1600.7 (w), 1585.7 (w), 1556.8 (vw), 1482.5 (w), 1471.4 (vw), 1293.5 (vw), 1272.3 (m), 1224.6 (w), 1152.7 (w), 1148.9 (vw), 1133.0 (vw), 1014.9 (vw), 826.3 (vw), 756.0 (w), 688.5 cm^{-1} (vw).

4-Diazo-2-methylbenzo-2,5-cyclohexadienone (5g). Compound **5g** was synthesized from 2-methyl-1,4-naphthoquinone following a literature procedure.[17] IR (Ar, 10 K): 2062.0 (vs), 2052.4 (m), 1635.8 (s), 1605.9 (s), 1600.6 (w), 1484.0 (m), 1472.4 (vw), 1380.3 (vw), 1304.1 (s), 1224.6 (vw), 1211.1 (m), 1201.1 (vw), 1111.3 (vw), 1073.7 (vw), 1037.0 (vw), 1033.7 (w), 1014.9 (vw), 941.6 (vw), 756.4 (w), 694.7 cm^{-1} (vw).

Matrix Spectroscopy. Matrix-isolation experiments were performed by standard techniques with an Air Products CSW-202 Displex closed cycle helium cryostat.[12e] Argon (Linde, 99.9999%) or a mixture of oxygen (Messer Griesheim, 99.998%) and argon (0.5% O_2) was deposited at 30 K on top of a CsI (IR) or sapphire (UV–vis) window with a rate of approximately 0.15 mmol/min. Quinone diazides **5b** and **5e** were warmed to 40 °C and codeposited. For the deposition of diazo compounds **5c,d,f,g**, which are less volatile, an electrically heated oven with a small distance between sample and window was utilized. Sample temperatures at deposition were 60, 65, 40, 40 °C for **5c,d,f,g**, respectively. Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer. Standard spectra were taken with a resolution of 1 cm^{-1} in the range 4000–500 cm^{-1}. UV–vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with a resolution of 2 nm. Irradiations were carried out with use of Osram HBO 500 W/2 mercury high-pressure arc lamps in an Oriel housing equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10-cm path of water and by a Schott KG1 filter. For broad-band irradiation, Schott cut-off filters were used (50% transmission at the wavelength specified); for narrow-band irradiation, interference filters (Schott) in combination with cut-off filters to isolate mercury lines were used.

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(21) The set up for matrix isolation is described in ref 12e. IR spectra were recorded on a Bruker IFS66 FT-IR spectrometer in the range 4000–450 cm^{-1}, the standard resolution was set to 1 cm^{-1}. Irradiation was performed by using a 500-W high-pressure mercury arc lamp, dichroic mirrors to preselect the range of irradiation and appropriate cut-off filters.
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Regiochemistry on Photoamination of Stilbene Derivatives with Ammonia via Electron Transfer

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The regiochemistry of photoamination of 1,2-diarylethene (1) with ammonia in the presence of *p*-dicyanobenzene (DCNB) has been investigated. The photoamination of stilbene and *p,p'*-dimethoxystilbene gave 1-amino-1,2-diphenylethane and 1-amino-1,2-bis(*p*-methoxyphenyl)ethane, respectively. The photoamination of unsymmetric 1-aryl-2-phenylethene having an alkoxy group on the para position occurred selectively to give 1-amino-2-aryl-1-phenylethane. On the other hand, the photoamination of 1-aryl-2-phenylethene having a methyl and chloro group on the para position or methoxy group on the meta and ortho positions gave both 1-amino-2-aryl-1-phenylethane and 1-amino-1-aryl-2-phenylethane. The regiochemistry is related with the distribution of positive charge in the cation radicals of 1 generated from photochemical electron transfer to DCNB.

Nucleophilic addition induced by photochemical electron transfer has received much attention as a potentially useful procedure for organic synthesis.[1] Especially regio- and stereoselective photoinduced nucleophilic additions have high synthetic potential. The regiochemistry for anti-Markovnikov addition of nucleophiles to aryl-substituted alkenes[2,3] (e.g., 1,1-diphenylethylene) and aryl-

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0022-3263/92/1957-1351$03.00/0

Table I. Photoamination of 1 with Ammonia[a]

1 ($E_{1/2}^{ox}$ (V))[b]	solvent[c]	irradn time (h)	yield[d] (%)	isomer ratio (2:3)	recov of 1 (%) (Z:E)	recov of DCNB (%)
1a (1.10)	9:0:1	20	46		14 (9:1)	97
1a	7:2:1	31	88		3 (1:1)	96
1b (0.91)	9:0:1	7	59	(1:0.4)	0	97
1c (1.06)	9:0:1	10	80	(1:0.7)	1 (1:1)	99
1c	8:1:1	20	91	(1:0.7)	2 (1:1)	91
1d (0.79)	9:0:1	21	53	(1:0)	6 (2:1)	97
1d	8:1:1	15	62	(1:0)	12 (4:1)	89
1e (0.68)	9:0:1	20	21	(1:0)	69 (4:1)	88
1f (0.75)	8:1:1	20	21	(1:0)	21 (2:1)	100
1g (1.09)	9:0:1	20	28	(1:0.7)	7 (5:1)	75
1g	7:2:1	17	60	(1:0.7)	2 (2:1)	82
1h (0.72)	9:0:1	20	0		70 (5:1)	88
1i (0.99)	7:2:1	20	87	(1:0.6)	0	92
1j (1.13)	7:2:1	8	54	(1:0.9)	6 (1:2)	100
1k (0.64)	7:2:1	41	44		5 (2:1)	100
1l (0.79)	7:2:1	20	16	(1:0)	59 (1:0)	85

[a] A MeCN–benzene–H_2O solution (70 mL) containing 1 (7 mmol) and DCNB (7 mmol) was bubbled with ammonia and then irradiated. [b] Half-peaks of oxidation potentials vs $Ag/AgNO_3$ for the trans isomer of 1. [c] The values are the ratio of MeCN–benzene–H_2O. [d] Isolated yields based on 1 used.

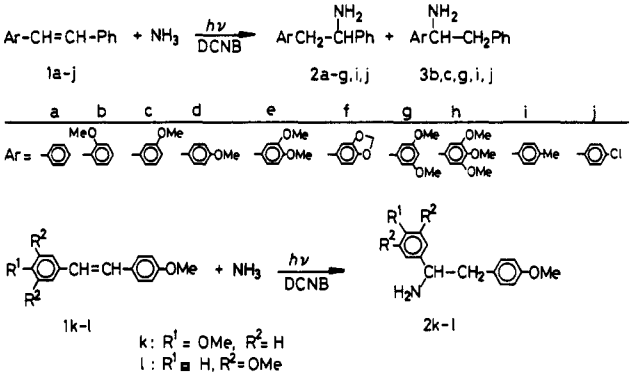
substituted cyclopropane[4] has been attributed to the conjugative stabilization by aryl groups for the adduct radicals (or cation radicals) formed form the reaction of nucleophile with the cation radicals. However, there are few studies on the regiochemistry of the photoinduced nucleophilic addition to the delocalized cation radicals such as arenes and stilbene derivatives,[5] since the addition of typical nucleophiles such as alcohols to the cation radicals is very inefficient.[6]

As a part of out studies on photoinduced nucleophilic addition, we have reported on photoamination of such electron-rich substrates as arenes[7] and 1,1-diarylalkenes[3] with ammonia and alkylamines. Recently, we applied the photoamination of stilbene to the synthesis of isoquinoline compounds such as benzylisoquinolines or isopavines.[8] Thus, ammonia and amines are such relatively strong nucleophiles that they can add the delocalized cation radicals. Therefore, we report here on the regiochemistry on the photoinduced nucleophilic addition to a dozen 1,2-diarylethenes using ammonia as nucleophile.

Results

The photoamination of 1,2-diarylethenes (**1a–l**) with ammonia was carried out by irradiating a degassed acetonitrile–water or acetonitrile–benzene–water solution containing **1a–l**, *p*-dicyanobenzene (DCNB), and ammonia through a Pyrex filter by a high-pressure mercury lamp at room temperature (Scheme I). An incident light was almost absorbed by 1 under these conditions. Upon the irradiation the isomerization from *trans*-1 to *cis*-1 immediately occurred up to the photostationary state where cis isomers are rich. Therefore, a mixture of cis and trans isomers of 1 was used for photoaminations. After the photoamination, DCNB was mostly recovered. No photoamination in the absence of DCNB occurred at all. The results of photoamination are summarized in Table I. The photoamination proceeded in relatively good yields whereas the photoaminations of **1e,f,l** proceeded in poor yields. But no photoamination of **1h** occurred. It should be noted that the photoamination proceeds in MeCN–benzene–H_2O (8:1:1 and 7:2:1) more efficiently than in MeCN–H_2O (9:1).

Scheme I



The photoamination of stilbene (**1a**) and *p,p'*-dimethoxystilbene (**1k**) gave 1-amino-1,2-diphenylethane (**2a**) and 1-amino-1,2-bis(*p*-methoxyphenyl)ethane (**2k**), respectively. The photoaminations of 1-aryl-2-phenylethenes **1b,c,g** having the methoxy group at the ortho or meta position gave both 1-amino-2-aryl-1-phenylethane **2** and 1-amino-1-aryl-2-phenylethane **3** in a ratio of 1:0.4–0.9. On the other hand, the photoamination of *p*-methoxystilbene (**1d**) gave 1-amino-2-(*p*-methoxyphenyl)-1-phenylethene (**2d**) selectively in contrast with the case of *p*-methyl or *p*-chlorostilbenes (**1i,j**) which gave both **2** and **3**. Similarly, the photoamination of **1e–f** having an alkoxy group at the para position gave the corresponding 1-amino-2-aryl-1-phenylethanes (**2e–f**) selectively. Also, the photoamination of 1-(*p*-methoxyphenyl)-2-(3,5-dimethoxyphenyl)ethene (**11**) with ammonia gave selectively 1-amino-1-(3,5-dimethoxyphenyl)-2-(*p*-methoxyphenyl)ethane (**21**).

Discussion

Stern–Volmer quenching studies show that DCNB quenches the excited singlet state of 1 (^{1}**1***) at a nearly diffusion-controlled rates, and the free energy changes for the electron transfer from ^{1}**1*** to DCNB are calculated to be negative by the Rehm–Weller equation[9] using the ox-

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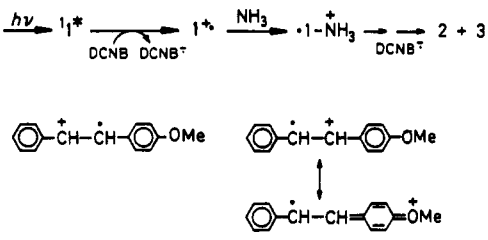
Scheme II



idation potentials ($E_{1/2}^{ox}$) of Table I. Therefore, the photoamination is certainly initiated by photochemical electron transfer from ^{1}1* to DCNB to give the cation radical of 1 (1$^{\cdot+}$) and the anion radical of DCNB (DCNB$^{\cdot-}$). As has been discussed earlier for arenes,[10] the nucleophilic addition of ammonia to 1$^{\cdot+}$ gives the aminated cation radicals, which are deprotonated and undergo reduction by DCNB$^{\cdot-}$ followed by protonation to afford the final aminated products **2** and/or **3**.

The positive charge of 1$^{\cdot+}$ might develop over two benzylic positions and aromatic rings, depending on the substituent on aryl group. In the cation radicals of **1d** having methoxy group at the para position, the positive charge might populate at benzylic position of the phenyl group more than at benzylic position of the *p*-methoxyphenyl group, since the photoamination occurred selectively at the benzylic position of phenyl group. The positive charge on the benzylic position of the *p*-methoxyphenyl group decreases by the resonance with the methoxy group at the para position which results in the localization of positive charge on the oxygen of methoxy groups (Scheme II). Similarly, the positive charge on the cation radicals of **1e–f** might populate at the benzylic position of the phenyl group more than at the benzylic position of the aryl groups to result in the selective photoamination. The inefficient photoaminations of **1e,f,h** arise from the fact that the positive charge of the cation radicals distributes over the aryl groups more predominantly than the olefinic moiety. In the case of the other stilbene derivatives **1b,c,g,i,j**, the positive charge might develop over both the benzylic positions of aryl and phenyl groups, resulting in formation of both **2** and **3**. Thus, it is found that the methoxy group on the para position affects strongly the regioselectivity for the photoamination of stilbene derivatives.

Experimental Section

^{1}H and ^{13}C NMR spectra were taken on a Bruker AC-250P for $CDCl_3$ solutions with tetramethylsilane used as an internal standard. Fluorescence spectra were taken on a Hitachi MPF-4. Fluorescence lifetimes were measured on a Horiba NAES 550 by a single-photon counting method. Oxidation potentials were measured in acetonitrile on a Hokuto Denko HA-501G and HB-105 as potentiostat and function generator using a three-electrode cyclic voltammetric cell; the working electrode, platinum disk; the counter electrode, carbon electrode; the reference electrode, Ag/$AgNO_3$. A JEOL JMS-D-300S was used for analyzing the mass spectra. GLC analysis was carried out on a Shimadzu GC-14A or GC-8A using a capillary column (CBP1-M25-025) or a 50-cm × 4-mm column of 2% silicone OV-17 on Chromosorb WAW DMCS.

Spectral-grade acetonitrile was distilled from P_2O_5 and then from CaH_2. Commercially available *p*-dicyanobenzene was used after recrystallization from methanol. The preparation of stilbene derivatives (**1b–l**) was performed by Wittig reaction of substituted benzaldehydes with phosphonium salts according to the literature method[11] except for the commercially available *trans*-**1a**.

***trans*-1b**: mp 56–57 °C (from hexane–benzene) (lit.[11] mp 58.6–59.5 °C); ^{13}C NMR δ 55.52, 110.96, 120.75, 123.52, 126.42, 126.47, 126.56, 127.34, 128.58, 128.65, 129.11, 137.98, 156.94.

***trans*-1c**: mp 37–38 °C (from hexane–benzene); ^{13}C NMR δ 55.24, 111.74, 113.29, 119.24, 126.54, 127.68, 128.57, 128.68, 129.00, 129.63, 137.21, 138.78, 159.88. Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.57; H, 6.60.

***trans*-1d**: mp 135–137 °C (from hexane–benzene) (lit.[11] mp 136.2–137.0 °C); ^{13}C NMR δ 55.32, 114.17, 126.26, 126.67, 127.21, 127.72, 128.23, 128.64, 130.21, 137.70, 159.36.

***trans*-1e**: mp 129–130 °C (from methanol); ^{13}C NMR δ 55.85, 55.93, 108.72, 111.20, 119.89, 126.27, 126.81, 127.29, 128.45, 128.66, 130.44, 137.51, 148.92, 149.11. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.95; H, 6.69.

***trans*-1f**: mp 96.2–96.5 °C (from benzene); ^{13}C NMR δ 101.12, 105.56, 108.42, 121.47, 126.31, 127.02, 127.36, 129.35, 129.66, 131.89, 137.41, 147.31, 148.15. Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.25. Found: C, 80.20; H, 5.35.

***trans*-1g**: mp 59–60 °C (from methanol); ^{13}C NMR δ 55.37, 100.02, 104.62, 126.58, 127.73, 128.68, 129.22, 137.15, 139.37, 161.00. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.67. Found: C, 79.84; H, 6.67.

***trans*-1h**: mp 109–110 °C (from benzene); ^{13}C NMR δ 56.18, 60.97, 103.76, 126.45, 127.60, 128.24, 128.71, 133.13, 137.27, 138.15, 153.47. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.48; H, 6.69.

***trans*-1i**: mp 122–122.5 °C (from hexane–benzene) (lit.[12] mp 119.2–119.8 °C); ^{13}C NMR δ 21.45, 126.39, 126.41, 127.39, 127.67, 128.63, 129.39, 134.52, 137.49.

***trans*-1j**: mp 132.5–133.0 °C (from hexane–benzene) (lit.[12] mp 129.2–129.6 °C); ^{13}C NMR δ 126.54, 127.34, 127.65, 127.86, 128.73, 128.83, 129.29, 133.16, 135.83, 136.96.

***trans*-1k**: mp 218–220 °C (from methanol) (lit.[12] mp 212–213.5 °C); ^{13}C NMR δ 55.32, 114.12, 126.20, 127.42, 130.51, 159.03.

***trans*-1l**: mp 56.5–57.5 °C (from methanol); ^{13}C NMR δ 55.34, 99.61, 104.33, 114.14, 126.56, 127.80, 128.74, 129.92, 139.70, 159.39, 160.96. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.40; H, 6.70.

Photoamination of 1a–l. General Procedure. In 140 mL of acetonitrile–water (9:1) or acetonitrile–benzene–water (7:2:1 or 8:1:1) was dissolved a mixture of **1** (7 mmol) and DCNB (7 mmol), and then ammonia gas was bubbled into the solutions. The solutions were irradiated with an Eikosha PIH-300 high-pressure mercury lamp through Pyrex under cooling with water. Details of the followup process was described in a literature.[7] We could not separate the acetamides of **2** and **3** by column chromatography on silica gel or recrystallization. Therefore, the assignments of **2** and **3** were performed by the ^{13}C NMR spectra.

Acetamide of 2a: mp 143–144 °C (from hexane–benzene); ^{1}H NMR δ 1.91 (3 H, s), 3.09 (2 H, d, J = 7.2 Hz), 5.26 (1 H, q, J = 7.2 Hz), 6.06 (1 H, br s), 7.03–7.06 (2 H, m), 7.18–7.36 (8 H, m); ^{13}C NMR δ 23.25, 42.52, 54.55, 126.56, 126.66, 127.40, 128.33, 128.55, 129.30, 137.34, 141.50, 169.37; MS m/e 239 (M^+) 196 (M – Ac) 148 (M – $PhCH_2$).

Acetamide of 2b: mp 136–137 °C (from hexane–benzene); ^{13}C NMR δ 23.34, 41.65, 54.44, 55.16, 113.71, 126.66, 127.31, 127.82, 128.50, 129.28, 130.26, 141.63, 158.23, 169.28. Anal. Calcd for $C_{17}H_{19}O_2N$: C, 75.81; H, 7.11; N, 5.20. Found: C, 76.02; H, 7.13; N, 5.21.

Acetamide of 3b: ^{13}C NMR δ 23.34, 42.46, 53.94, 55.24, 113.88, 126.50, 128.50, 129.30, 129.31, 133.70, 137.52, 158.77, 169.20.

Acetamide of 2c: ^{13}C NMR δ 23.39, 42.53, 54.26, 55.08, 112.27, 114.75, 121.66, 127.41, 128.55, 129.29, 138.76, 141.46, 159.49, 169.26.

Acetamide of 3c: ^{13}C NMR δ 24.02, 42.47, 54.36, 55.20, 112.60, 112.67, 118.84, 126.53, 128.33, 129.60, 137.26, 143.15, 159.69, 169.26.

Acetamide of 2d: mp 145–146 °C (from methanol); ^{1}H NMR δ 1.96 (3 H, s), 3.06 (2 H, d, J = 7.1 Hz), 3.77 (3 H, s), 5.23 (1 H, dt, J = 7.3 and 7.6 Hz), 6.06 (1 H, br d), 6.77 (2 H, d, J = 8.6 Hz), 6.97 (2 H, d, J = 8.6 Hz), 7.20–7.35 (m, 5 H); ^{13}C NMR δ 23.26, 41.63, 54.72, 55.20, 113.78, 126.69, 127.56, 128.56, 129.24, 130.29, 141.51, 158.33, 169.45; MS m/e 269 (M^+), 226 (M – Ac), 211 (M – NHAc). Anal. Calcd for $C_{17}H_{19}NO_2$; H, 7.11; C, 75.81; N, 5.20.

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Found: H, 7.07; C, 75.55; N, 5.18.

Acetamide of 2e: mp 140–141 °C (from methanol); ^{1}H NMR δ 1.97 (3 H, s), 3.03 (1 H, dd, J = 13.6 and 7.1 Hz), 3.09 (1 H, dd, J = 13.6 and 6.4 Hz), 3.70 (3 H, s), 3.83 (3 H, s), 5.24 (1 H, q, J = 7.1 Hz), 5.89 (1 H, br d), 6.42 (1 H, s), 6.59 (1 H, d, J = 8.1 Hz), 6.75 (1 H, d, J = 8.1 Hz), 7.17–7.30 (3 H, m); ^{13}C NMR δ 23.38, 42.11, 54.52, 55.72, 55.86, 111.07, 112.62, 121.42, 126.75, 127.42, 128.58, 129.58, 141.39, 147.81, 148.71, 169.34; MS m/e 299 (M^+), 241 (M – NHAc). Anal. Calcd for $C_{18}H_{21}NO_3$: H, 7.07; C, 72.21; N, 4.68. Found: H, 7.02; C, 71.98; N, 4.63.

Acetamide of 2f: ^{1}H NMR δ 1.96 (3 H, s), 3.02 (2 H, d, J = 7.08 Hz), 5.20 (1 H, q, J = 7.6 Hz), 5.88 (1 H, br d), 5.90 (2 H, s), 6.00 (d, J = 7.7 Hz), 6.53 (1 H, s), 6.67 (1 H, d, J = 7.7 Hz), 7.16–7.37 (5 H, m); ^{13}C NMR δ 23.42, 42.21, 54.64, 100.85, 108.07, 109.61, 122.31, 126.64, 127.46, 128.60, 130.99, 141.35, 146.21, 147.54, 169.29; MS m/e 282 (M – 1), 223.

Acetamide of 2g: ^{13}C NMR δ 23.04, 42.82, 54.47, 55.12, 98.73, 107.33, 126.73, 127.19, 128.41, 140.00, 142.00, 160.60, 169.71.

Acetamide of 3g: ^{13}C NMR δ 22.98, 42.60, 54.81, 55.18, 99.02, 104.97, 126.41, 128.23, 129.24, 137.78, 144.54, 160.82, 169.71.

Acetamide of 2i: ^{13}C NMR δ 21.03, 23.37, 42.06, 54.38, 126.63, 127.34, 128.52, 129.04, 129.16, 134.05, 136.07, 141.58, 169.35.

Acetamide of 3i: ^{13}C NMR δ 21.07, 23.37, 42.41, 54.18, 126.50, 126.57, 128.30, 129.24, 129.31, 137.06, 137.42, 138.40, 169.29.

Acetamide of 2j: ^{13}C NMR δ 23.38, 41.76, 54.53, 126.69, 127.65, 128.68, 130.63, 132.38, 135.80, 140.90, 169.38.

Acetamide of 3j: ^{13}C NMR δ 23.31, 42.38, 53.85, 126.78, 128.01, 128.43, 128.48, 129.24, 133.09, 136.79, 140.09, 169.38.

Acetamide of 2k: mp 154–155 °C; ^{1}H NMR δ 1.93 (3 H, s), 2.99 (1 H, dd, J = 13.7 and 7.3 Hz), 3.06 (1 H, dd, J = 13.7 and 6.9 Hz), 3.77 (3 H, s), 3.79 (3 H, s), 5.17 (1 H, q, J = 7.3 Hz), 5.99–6.02 (1 H, br d, J = 7.8 Hz), 6.75–6.85 (4 H, m), 6.96 (2 H, d, J = 8.6 Hz), 7.13 (2 H, d, J = 6.4 Hz); ^{13}C NMR δ 23.32, 41.59, 54.14, 55.17, 55.25, 113.71, 113.90, 127.85, 129.48, 130.29, 133.70, 158.22, 158.79, 169.25; MS m/e 296, 241.

Acetamide of 2l: ^{1}H NMR δ 1.92 (3 H, s), 2.99 (2 H, d, J = 7.0 Hz), 3.73 (6 H, s), 3.76 (3 H, s), 5.15 (1 H, t, J = 7.0 Hz), 5.87 (1 H, br d), 6.26 (1 H, s), 6.34 (2 H, s), 6.76 (2 H, d, J = 8.6 Hz), 6.79 (2 H, d, J = 8.6 Hz); ^{13}C NMR δ 23.35, 41.54, 54.62, 55.32, 98.99, 104.89, 113.76, 130.27, 160.04, 129.24, 144.12, 169.36; MS m/e 329 (M^+), 270 (M – NH_2Ac).

Registry No. *trans*-**1a**, 103-30-0; *trans*-**1b**, 52805-92-2; *trans*-**1c**, 14064-41-6; *trans*-**1d**, 1694-19-5; *trans*-**1e**, 3892-92-0; *trans*-**1f**, 51003-16-8; *trans*-**1g**, 21956-56-9; *trans*-**1h**, 74809-43-1; *trans*-**1i**, 1860-17-9; *trans*-**1j**, 1657-50-7; *trans*-**1k**, 15638-14-9; *trans*-**1l**, 22255-22-7; **2a** acetamide derivative, 2155-90-0; **2b** acetamide derivative, 138435-22-0; **2c** acetamide derivative, 138435-23-1; **2d** acetamide derivative, 93172-54-4; **2e** acetamide derivative, 76306-60-0; **2f** acetamide derivative, 76306-61-1; **2g** acetamide derivative, 138435-24-2; **2i** acetamide derivative, 138435-25-3; **2j** acetamide derivative, 138435-26-4; **2k** acetamide derivative, 93172-56-6; **2l** acetamide derivative, 138435-27-5; **3b** acetamide derivative, 138435-28-6; **3c** acetamide derivative, 138435-29-7; **3g** acetamide derivative, 138435-30-0; **3i** acetamide derivative, 138435-31-1; **3j** acetamide derivative, 138458-90-9.

Supplementary Material Available: ^{1}H NMR spectra for the acetamides of **2a–g,i–l** and **3b,c,e,g,i,j** (24 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Force Field Modeling of Transition Structures of Intramolecular Ene Reactions and ab Initio Transition Structures for an Activated Enophile

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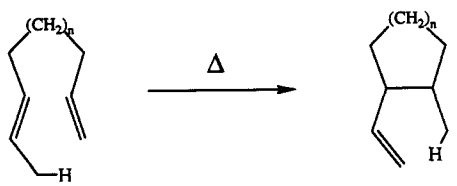
A modification of Allinger's MM2 force field has been developed to rationalize and predict the stereochemistries of intramolecular ene reactions. This force field reproduces the stereochemical trends observed for intramolecular ene reactions with unactivated enophiles, but gives poor results with activated enophiles. Ab initio molecular orbital calculations on the ene reaction of acrylonitrile with propene were performed to investigate the change in the transition structure caused by activating substituents.

Introduction

The intramolecular ene reaction[1,2] has been used frequently in organic synthesis for the formation of five- and six-membered rings, with control of the stereochemistry in the products. With activating substituents and catalysis by Lewis acids, reaction temperatures are usually lower and there is greater control of stereochemistry than in simple hydrocarbon cases.[3,4] The stereochemistry about the forming CC bond is usually cis for five-membered rings and trans for six-membered rings. The relationship between the stereochemistries of substituents on the tether and the stereochemistry of CC bond formation is not as easily predicted. In this paper, we present a simple modification of Allinger's MM2 force field[5] which models the transition structures of intramolecular ene reactions



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