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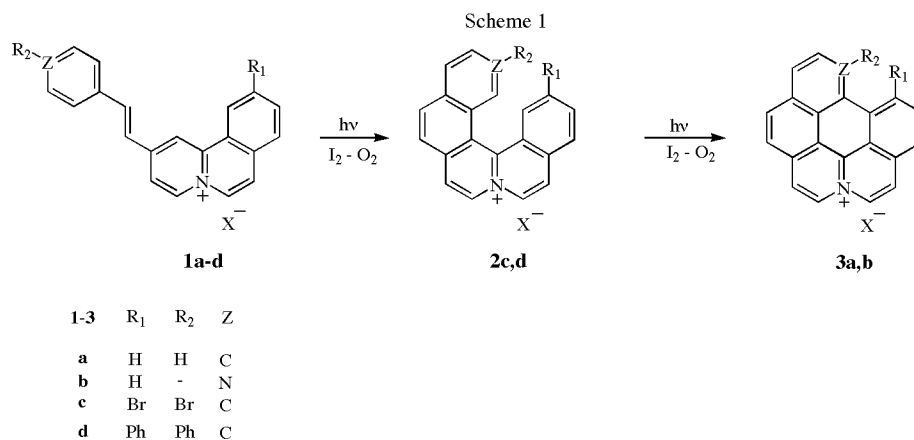
Oxidative photocyclization of 4-(2-arylviny)benzo[*a*]quinolizinium salts (**6**) gave five- or six-membered rings depending on the aryl substituent. The olefins **6a** and **6b** with a phenyl or naphthyl substituent resulted in a normal six-membered ring formation to afford 6a-azoniapicene and 6a-azoniabenzob[*b*]picene salts (**7** and **8**), respectively. In contrast, the photo-reaction of pyridyl substituted derivative **6c** resulted in novel five-membered ring formation to yield 3b-azonia-5-(2-pyridyl)acephenanthrylene salt (**10**).

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The oxidative photocyclization is a useful synthetic method to construct various polycyclic azonia-aromatic ring systems with a bridgehead quaternary nitrogen [2]. For example, we have already reported that the oxidative photocyclization of 2-(2-arylviny)benzo[*a*]quinolizinium salts (**1a-d**) afforded azonia[5]helicenes (**2c, d**) or the azonia derivatives of benzo[*ghi*]perylene (**3a, b**) depending on the aryl substituents (Scheme 1) [2c,3]. On the other hand the oxidative photocyclization of 4-(2-arylviny)benzo[*a*]quinolizinium salts (**6**) appeared to be a reasonable synthetic approach for previously unknown azonia derivatives of picene. Unexpectedly in the photo-reaction of 4-[2-(2-pyridyl)viny]benzo[*a*]quinolizinium salt (**6c**), novel five-membered ring formation was observed and is reported herein.

new peak appeared at 403 nm. After work-up a yellow product was obtained. The fab-ms spectrum exhibited a molecular ion peak at *m/z* 280: this pointed to the loss of two hydrogens from **6a**. ¹H Nmr spectrum showed three two-spin systems and two four-spin systems, which can be unambiguously assigned by H-H COSY spectrum. These results indicate that the photocyclization product is a desired new 6a-azoniapicene perchlorate (**7**) (45 % yield). Similarly, irradiation of the olefin (*E*)-**6b** in the presence of iodine in methanol led to previously unknown 6a-azoniabenzob[*b*]picene perchlorate (**8**) in 50 % yield.

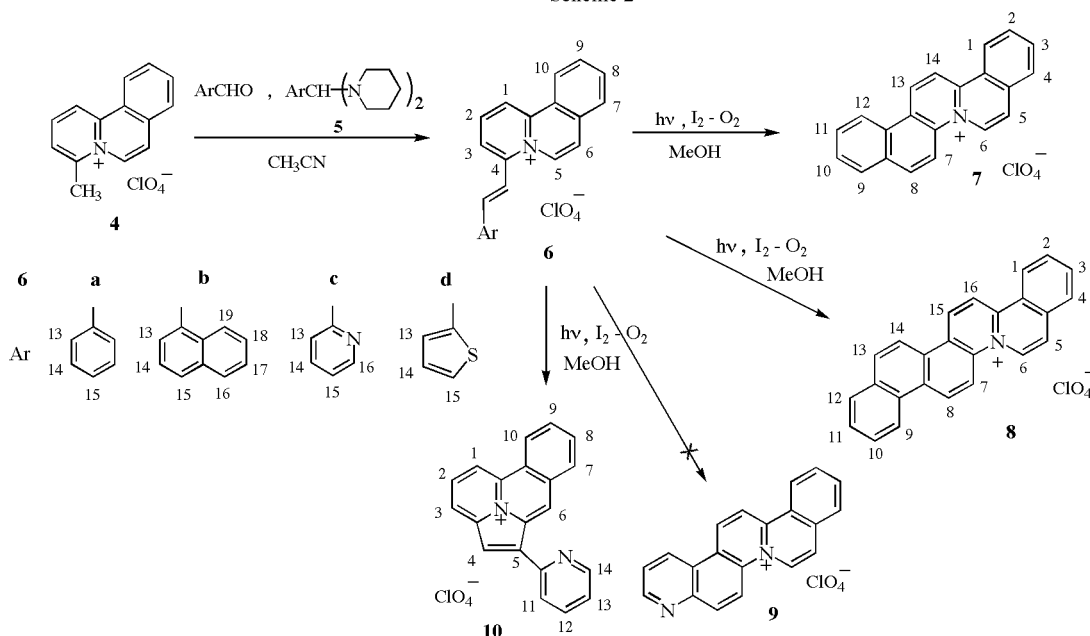
The irradiation of an aerated methanol solution of the olefin (*E*)-**6c** in the presence of iodine led to isolation of a yellow product. The molecular ion (*m/z* 281) by fab-ms



The (*E*)-4-(2-arylviny)benzo[*a*]quinolizinium salts (**6a-d**) were obtained in 81-98 % yields by the condensation reaction of 4-methylbenzo[*a*]quinolizinium perchlorate (**4**) [4] with benzaldehyde derivatives under improved Knoevenagel conditions [5] using aminal **5** and acetonitrile as a solvent (Scheme 2). When an aerated methanol solution of (*E*)-4-styrylbenzo[*a*]quinolizinium salt (**6a**) and iodine was irradiated with a high-pressure mercury lamp through a Pyrex-filter, the first absorption band at 378 nm hypsochromically shifted to 372 nm, and then a

corresponded to that of the expected 9-aza-6a-azoniapicene salt (**9**). The ¹H nmr spectrum of compound **9** should show three two-spin systems, one three-spin system, and one four-spin system. However, the ¹H nmr spectrum of the yellow product was not consistent with the structure **9**, because it revealed two singlets at δ 8.57 and 10.29, two four-spin systems, and one three-spin system. One of the four-spin systems was assigned to 2-substituted pyridine on the basis of the coupling constants and the chemical shifts. The uv spectrum of the yellow product

Scheme 2

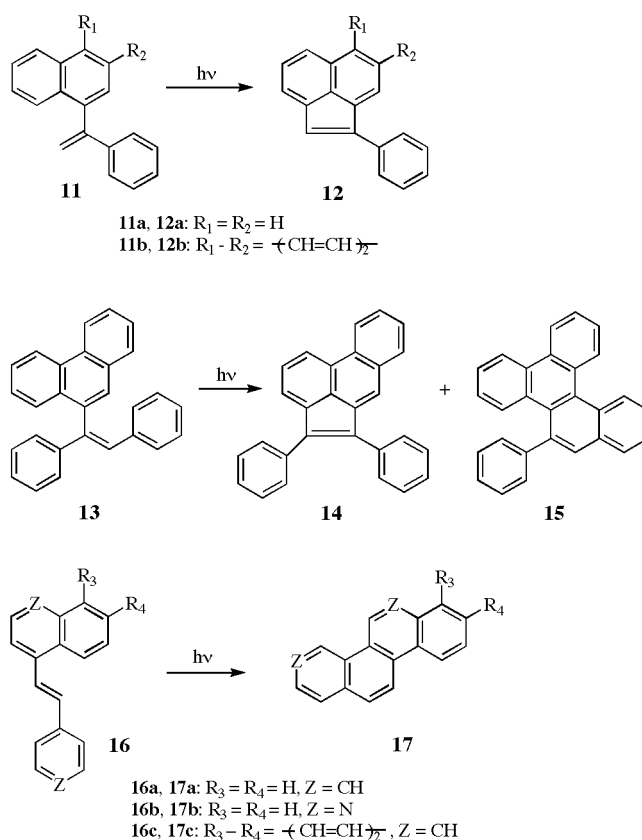


also exhibited no spectral resemblance to 6a-azoniapicene salt (**7**). From these results the structure was concluded to be 3b-azonia-5-(2-pyridyl)acephenanthrylene perchlorate (**10**) (57 % yield).

Although the oxidative photocyclization of the olefins **6a** and **6b** provided normal six-membered ring formation, the photocyclization of the olefin **6c** with a 2-pyridyl group resulted in novel five-membered ring formation. Therefore photocyclization of the olefin (*E*)-**6d** with a π -excessive thiophene ring was examined. An aerated methanol solution of the olefin (*E*)-**6d** in the presence of iodine was irradiated with a Pyrex-filtered light to afford *E*-*Z* mixtures of starting material and no cyclization products were observed.

Only a few examples have been reported on the five-membered ring formation by photocyclization (Scheme 3). The oxidative photocyclization of 1,1-diarylethylenes gave a five-membered ring: photo-reaction of 1-(1-phenylvinyl)naphthalene (**11a**) and 9-(1-phenylvinyl)phenanthrene (**11b**) gave 4-phenylacenaphthylene (**12a**: 70% yield) [6] and 5-phenylacephenanthrylene (**12b**: 1% yield) [7], respectively. The photocyclization of 1,1,2-triarylethylene **13** have been reported to yield a five-membered product (**14**: 1% yield) with a six-membered product (**15**: 80% yield) [7]. On the other hand the photo-reaction of 1,2-diarylethylenes, such as 1-styrylnaphthalene (**16a**), its aza derivative (**16b**), and 1-styrylphenanthrene (**16c**) gave the normal photocyclization products chrysene (**17a**: 77% yield) [8], its aza derivative (**17b**: 25% yield) [9], and picene (**17c**: 61% yield) [10], respectively. To the best of our knowledge, our result is the first example for the five-membered ring formation from 1,2-diarylethylene derivative.

Scheme 3



Further studies on the photocyclization of 4-(2-arylviny)benzo[*a*]quinolinium salts are in progress.

EXPERIMENTAL

Melting points were determined on a Yamato melting point apparatus MP-21 and are uncorrected. U.v. spectra were obtained with a Hitachi 220A spectrophotometer. ^1H Nmr spectra were measured with a JEOL-EX 270 (270 MHz) or EX400 (400 MHz) spectrometers using tetramethylsilane as internal standard. Chemical shifts were measured in ppm downfield from the internal standard. Spectral assignments are supported by H-H COSY spectra. Protons are labeled as shown in Schemes. Fast-atom bombardment (fab) mass spectra were recorded with a JEOL JMS-DX300 spectrometer with *m*-nitrobenzyl alcohol as matrix. The elemental analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. An Eikosha 300W or Ushio 450W high-pressure mercury lamp was used as the irradiation source. Thin layer chromatography was performed on cellulose-coated Merk 5552-1M plates. 4-Methylbenzo[*a*]quinolizinium perchlorate (**4**) was prepared by photocyclization of 1-styryl-2-methylpyridinium salt according to our previous paper [4]. The amins **5** were prepared from arylaldehyde and piperidine according to our literature procedure [5].

General Procedure for the Preparation of the (*E*)-4-(2-Arylvinyl)benzo[*a*]quinolizinium Perchlorates (**6a-d**).

To a refluxing acetonitrile solution (25 mL) of 4-methylbenzo[*a*]quinolizinium perchlorate (**4**) (3.4 mmoles) and the respective arylaldehyde (10 mmoles), the amina (**5**) (1.7 mmoles) was added. The mixture was refluxed for 1 hour. After cooling of the mixture to room temperature, diethyl ether (150 mL) was added. The resulting precipitate was isolated by filtration, washed with ether, and dried *in vacuo* to give (*E*)-4-(2-arylvinyl)benzo[*a*]quinolizinium perchlorates **6a-d**. Analytically pure samples were obtained by recrystallization.

(*E*)-4-(2-Phenylvinyl)benzo[*a*]quinolizinium Perchlorate (**6a**).

This compound was obtained as pale yellow crystals (ethyl acetate-ethanol), yield 92 %, mp 241° dec; uv (methanol): λ_{max} 378 (log ϵ 4.31), 316 (4.35), 280 (sh), and 232 nm (4.50); ^1H nmr (270 MHz, dimethyl sulfoxide- d_6): δ 7.49-7.55 (m, 2H, 14- and 15-H), 7.80 (d, 1H, vinyl-H, $J = 15.6$ Hz), 7.94 (d, 1H, 13-H, $J = 6.6$ Hz), 8.03 (d, 1H, vinyl-H, $J = 15.6$ Hz), 8.07-8.20 (m, 2H, 8- and 9-H), 8.34-8.40 (m, 2H, 6- and 7-H), 8.56 (d, 1H, 3-H, $J = 7.6$ Hz), 8.68 (dd, 1H, 2-H, $J = 7.6$ and 8.3 Hz), 9.21 (d, 1H, 10-H, $J = 7.9$ Hz), 9.33 (d, 1H, 5-H, $J = 7.8$ Hz), 9.52 (d, 1H, 1-H, $J = 8.3$ Hz); fab-ms: m/z 282 (M-ClO $_4$) $^+$.

Anal. Calcd. for C $_{21}$ H $_{16}$ NClO $_4$: C, 66.06; H, 4.22; N, 3.67. Found: C, 65.88; H, 4.14; N, 3.67.

(*E*)-4-[2-(1-Naphthyl)vinyl]benzo[*a*]quinolizinium Perchlorate (**6b**).

This compound was obtained as yellow crystals (acetonitrile), yield 82 %, mp 311° dec; uv (methanol): λ_{max} 385 (log ϵ 4.25), 340 (4.08), 286 (4.27), 270 (sh), and 222 nm (4.84); ^1H nmr (400 MHz, dimethyl sulfoxide- d_6): δ 7.61-7.73 (m, 3H, 14-, 17-, and 18-H), 8.03-8.20 (m, 5H, 8-, 9-, 15-, 16-, and vinyl-H), 8.33-8.39 (m, 3H, 6-, 7-, and 13-H), 8.53 (d, 1H, 19-H, $J = 8.3$ Hz), 8.62 (d, 1H, vinyl-H, $J = 15.9$ Hz), 8.72 (dd, 1H, 2-H, $J = 7.8$ and 8.6 Hz), 8.80 (d, 1H, 3-H, $J = 7.8$ Hz), 9.23 (d, 1H, 10-H, $J = 8.3$ Hz), 9.39 (d, 1H, 5-H, $J = 7.3$ Hz), 9.54 (d, 1H, 1-H, $J = 8.6$ Hz); fab-ms: m/z 332 (M-ClO $_4$) $^+$.

Anal. Calcd. for C $_{25}$ H $_{18}$ NClO $_4$: C, 69.53; H, 4.20; N, 3.24. Found: C, 69.53; H, 4.12; N, 3.14.

(*E*)-4-[(2-(2-Pyridyl)vinyl)]benzo[*a*]quinolizinium Perchlorate (**6c**).

This compound was obtained as dark green crystals (acetonitrile), yield 98 %, mp 205-207° dec; uv (methanol): λ_{max} 371 (log ϵ 4.34), 310 (4.43), 280 (sh), and 230 nm (4.04); ^1H nmr (270 MHz, dimethyl sulfoxide- d_6): δ 7.49 (dd, 1H, 15-H, $J = 4.4$ and 6.9 Hz), 7.81 (d, 1H, vinyl-H, $J = 15.3$ Hz), 7.88 (d, 1H, 13-H, $J = 7.6$ Hz), 7.99 (dd, 1H, 14-H, $J = 6.9$ and 7.6 Hz), 8.11 (dd, 1H, 9-H, $J = 7.4$ and 8.0 Hz), 8.18 (dd, 1H, 8-H, $J = 7.3$ and 7.4 Hz), 8.33 (d, 1H, vinyl-H, $J = 15.3$ Hz), 8.37-8.42 (m, 2H, 6- and 7-H), 8.57 (d, 1H, 3-H, $J = 7.6$ Hz), 8.71 (dd, 1H, 2-H, $J = 7.6$ and 8.6 Hz), 8.76 (d, 1H, 16-H, $J = 4.4$ Hz), 9.19 (d, 1H, 5-H, $J = 7.4$ Hz), 9.23 (d, 1H, 10-H, $J = 8.0$ Hz), 9.56 (d, 1H, 1-H, $J = 8.6$ Hz); fab-ms: m/z 283 (M-ClO $_4$) $^+$.

Anal. Calcd. for C $_{20}$ H $_{15}$ N $_2$ ClO $_4$: C, 62.75; H, 3.95; N, 7.32. Found: C, 62.52; H, 4.01; N, 7.18.

(*E*)-4-[(2-(2-Thienyl)vinyl)]benzo[*a*]quinolizinium Perchlorate (**6d**).

This compound was obtained as yellowish brown needles (acetonitrile-ethanol), yield 81 %, mp 198-199° dec; uv (methanol): λ_{max} 394 (log ϵ 4.39), 330 (4.33), 278 (4.44), and 222 nm (4.54); ^1H nmr (270 MHz, dimethyl sulfoxide- d_6): δ 7.26 (dd, 1H, 14-H, $J = 2.6$ and 5.3 Hz), 7.68-7.73 (m, 2H, vinyl-H and 15-H), 7.83 (d, 1H, 13-H, $J = 5.3$ Hz), 8.02 (d, 1H, vinyl-H, $J = 15.7$ Hz), 8.09 (dd, 1H, 9-H, $J = 7.4$ and 8.3 Hz), 8.16 (dd, 1H, 8-H, $J = 7.3$ and 7.4 Hz), 8.34-8.38 (m, 2H, 6- and 7-H), 8.52 (d, 1H, 3-H, $J = 6.9$ Hz), 8.65 (dd, 1H, 2-H, $J = 6.9$ and 8.6 Hz), 9.19 (d, 1H, 10-H, $J = 8.3$ Hz), 9.27 (d, 1H, 5-H, $J = 7.6$ Hz), 9.48 (d, 1H, 1-H, $J = 8.6$ Hz); fab-ms: m/z 288 (M-ClO $_4$) $^+$.

Anal. Calcd. for C $_{19}$ H $_{14}$ NSClO $_4$: C, 58.84; H, 3.64; N, 3.61. Found: C, 58.63; H, 3.85; N, 3.45.

Typical Procedure for the Photocyclization of 4-(2-Arylvinyl)benzo[*a*]quinolizinium Perchlorates (**6a-c**).

A solution of the olefin (*E*)-**6** (0.25 mmol) and iodine (0.1 mmol) in methanol (1000 mL) was irradiated at room temperature with a 300 W high-pressure mercury lamp inside a Pyrex immersion well. The progress of the photocyclization was monitored by uv and visible spectra. When the spectra of the *Z* form of **6** had disappeared, irradiation was stopped, and the solvent was removed under reduced pressure. A thin layer chromatogram (cellulose: water: ethanol = 80:20) of the reaction mixture showed one spot. The residue was recrystallized to afford the photocyclization product.

6a-Azoniapicene Perchlorate (**7**).

This compound was obtained as yellowish needles by repeated recrystallization from acetonitrile-ethyl acetate, yield 45 %, mp 291-293° dec.; uv (methanol): λ_{max} 403 (log ϵ 4.45), 383 (4.23), 286 (4.64), and 239 nm (4.62); ^1H -nmr (270MHz, dimethyl sulfoxide- d_6): δ 7.96 (1H, dd, 10-H, $J = 9.2$, 6.8 Hz), 8.03 (1H, dd, 11-H, $J = 8.3$, 6.8 Hz), 8.16 (1H, dd, 2-H, $J = 8.6$, 7.3 Hz), 8.25 (1H, dd, 3-H, $J = 7.6$, 7.3 Hz), 8.35 (1H, d, 9-H, $J = 9.2$ Hz), 8.42 (1H, d, 4-H, $J = 7.6$ Hz), 8.59 (1H, d, 5-H, $J = 7.7$ Hz), 8.76 (1H, d, 8-H, $J = 9.6$ Hz), 9.20 (1H, d, 7-H, $J = 9.6$ Hz), 9.26 (1H, d, 12-H, $J = 8.3$ Hz), 9.43 (1H, d, 1-H, $J = 8.6$ Hz), 9.66 (1H, d, 14-H, $J = 9.6$ Hz), 10.01 (1H, d, 13-H, $J = 9.6$ Hz), and 10.12 (1H, d, 6-H, $J = 7.7$ Hz); fab-ms: m/z 280 (M-ClO $_4$) $^+$.

Anal. Calcd. for C $_{21}$ H $_{14}$ NClO $_4$: C, 66.41; H, 3.72; N, 3.69. Found: C, 66.24; H, 3.66; N, 3.60.

6a-Azoniabenzo[*b*]picene Perchlorate (**8**).

This compound was obtained as yellow crystals (acetonitrile), yield 50 %, mp > 330°; uv (methanol): λ_{\max} 407 (log ϵ 4.33), 390 (4.21), 323 (4.45), 283 (4.66), 280 (4.66), 260 (4.55), and 232 nm (4.53); ^1H nmr (400 MHz, dimethyl sulfoxide- d_6): δ 7.66 (1H, dd, 11-H, J = 7.7, 7.5 Hz), 7.76 (1H, dd, 10-H, J = 7.8, 7.5 Hz), 8.05 (1H, d, 12-H, J = 7.7 Hz), 8.14 (1H, dd, 2-H, J = 7.9, 7.5 Hz), 8.23 (1H, dd, 3-H, J = 7.6, 7.5 Hz), 8.27 (1H, d, 13-H, J = 9.3 Hz), 8.39 (1H, d, 4-H, J = 7.6 Hz), 8.54 (1H, d, 5-H, J = 7.6 Hz), 9.03 (1H, d, 9-H, J = 7.8 Hz), 9.04 (1H, d, 14-H, J = 9.3 Hz), 9.24 (1H, d, 7-H, J = 9.5 Hz), 9.34 (1H, d, 1-H, J = 7.9 Hz), 9.49 (1H, d, 16-H, J = 9.0 Hz), 9.51 (1H, d, 8-H, J = 9.5 Hz), 9.92 (1H, d, 15-H, J = 9.0 Hz), and 10.11 (1H, d, 6-H, J = 7.6 Hz); fab-ms: m/z 330 (M-ClO₄)⁺.

Anal. Calcd. for C₂₅H₁₆NClO₄: C, 69.85; H, 3.75; N, 3.26. Found: C, 70.00; H, 3.71; N, 3.25.

3a-Azonia-5-(2-pyridyl)acephenanthrylene Perchlorate (**10**).

This compound was obtained as yellow crystals (acetone), yield 57 %; mp 292° dec.; uv (methanol): λ_{\max} 425 (log ϵ 3.66), 403 (3.82), 367 (4.09), 346 (4.02), 328 (4.00), 320 (4.23), 288 (4.39), 282 nm (4.35). ^1H nmr (270 MHz, dimethyl sulfoxide- d_6): δ 7.58 (1H, dd, 13-H, J = 7.8, 5.0 Hz), 8.06 (1H, dd, 12-H, J = 8.0, 7.8 Hz), 8.28 (1H, d, 11-H, J = 8.0 Hz), 8.32-8.38 (2H, m, 9-H and 8-H), 8.57 (1H, s, 4-H), 8.71 (1H, d, 7-H, J = 7.3 Hz), 8.85 (1H, d, 3-H, J = 7.9 Hz), 8.89-8.95 (2H, m, 2-H and 14-H), 9.32 (1H, d, 10-H, J = 7.6 Hz), 9.55 (1H, d, 1-H, J = 8.3 Hz), 10.29 (1H, s, 6-H); fab-ms: m/z 281 (M-ClO₄)⁺.

Anal. Calcd. for C₂₀H₁₃N₂O₄Cl: C, 63.09; H, 3.44; N, 7.36. Found: C, 63.00; H, 3.24; N, 7.28.

REFERENCES AND NOTES

- [1] Part 3 of the series "Photocyclization of Styrylbenzo[*a*]quinolinizinium Salts". For Part 2 see ref. [2c].
- [2a] S. Arai, T. Takeuchi, M. Ishikawa, T. Takeuchi, M. Yamazaki and M. Hida, *J. Chem. Soc., Perkin Trans.1*, 481 (1987); [b] S. Arai, T. Yafune, M. Ohkubo and M. Hida, *Tetrahedron Lett.*, **30**, 7217 (1989); [c] K. Sato, K. Nakajima, S. Arai and T. Yamagishi, *Liebigs Ann.*, 439 (1996); [d] S. Arai, T. Yamagishi and M. Hida, *Yuki Gosei Kagaku Kyokaishi (J. Syn. Org. Chem. Jpn.)*, **51**, 62 (1993).
- [3] S. Arai, N. Nakamura, H. Yamaguchi, M. Okazaki, and M. Hida, *Bull. Chem. Soc. Jpn.*, **64**, 1996 (1991).
- [4] S. Arai, M. Yamazaki, and M. Hida, *J. Heterocyclic Chem.*, **27**, 1073 (1990).
- [5] K. Sato, K. Kano, T. Yafune, M. Hida, S. Arai, and M. Hida, *Heterocycles*, **37**, 955 (1994).
- [6] R. Lapouyade, R. Koussini, and J.-C. Rayez, *J. Chem. Soc., Chem. Commun.*, 676 (1975).
- [7] W. H. Laarhoven and Th. J. H. M. Cuppen, *Rec. Trav. Chim. Pays-Bas*, **95**, 165 (1975).
- [8] C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964).
- [9] C. E. Loader and C. J. Timmons, *J. Chem. Soc. (C)*, 330 (1968).
- [10] R. J. Hayward and C. C. Leznoff, *Tetrahedron*, **27**, 5115 (1971).