products and to let the chemist/user participate in the screening.

VII. Conclusion

The capabilities of the CAMEO program have been extended to include ylide chemistry and organometallic reactions involving lithium, magnesium, and lithium cuprates. Related literature data were organized with particular attention to the competitions between proton transfer, organometallic addition, and halogen–metal exchange. Overall, the new chemistry merged readily into the existing program for base-catalyzed chemistry. The principal changes were in the routines for the perception of relative acidities and of nucleophiles. The program is constantly evolving and future publications will describe the progress in broadening the scope to other areas of synthetic organic chemistry including electrophilic and pericyclic reactions.

Acknowledgment. Gratitude is expressed to the National Science Foundation for support of this work and to Procter and Gamble, Inc. for a graduate fellowship awarded to D.M. The assistance and advice of Professor D. W. Brooks, Catherine E. Peishoff, Barbara L. Roos-Kozel, and Julia A. Schmidt are also appreciated. Special thanks go to Professor Phillip L. Fuchs for frequent synthetic consultation and for access to the synthetic literature retrieval program, PULSAR.[50]

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Exploitation of Solar Energy Storage Systems. Valence Isomerization between Norbornadiene and Quadricyclane Derivatives

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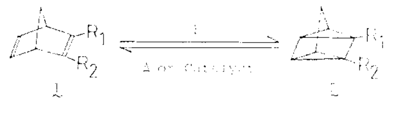
Use of copper(I)–nitrogen ligand catalysts such as $Ph_3PCuCl{\cdot}bpy$ (**3**), $Ph_3PCuCl{\cdot}phen$ (**4**), $Ph_3PCuCl{\cdot}phtha$ (**5**), and $Ph_3PCuBr{\cdot}py$ (**6**) enables the photochemical isomerization of norbornadiene to quadricyclane to be performed at a longer wavelength than 350 nm, at which CuCl catalyst itself cannot induce such an isomerization. Among the norbornadiene derivatives bearing various chromophores, 3-(phenylcarbamoyl)norbornadiene-2-carboxylic acid (**1f**) undergoes a facile and quantitative isomerization into the corresponding quadricyclane derivative (**2f**) in sunlight. The back-isomerization of **2f** to **1f** proceeds quantitatively by use of catalytic amounts of $Rh_2(CO)_4Cl_2$.

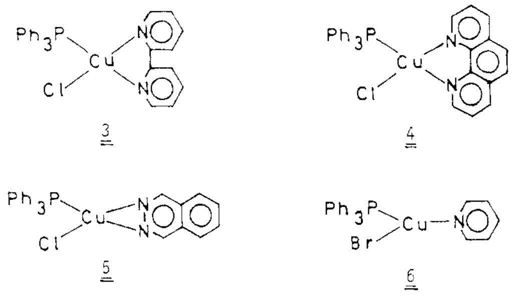
Exploitation of solar energy storage systems based on valence isomerization of organic materials has recently received wide attention.[1] Among many systems examined, norbornadiene[2] derivative (**1**)–quadricyclane[3] derivative (**2**) systems are very hopeful[1a,4-12] because of (i) the relatively large enthalpy change of the isomerization, (ii) quantitative chemical yields, (iii) stability of quadricyclane derivatives,[1a] and (iv) easy and clean back-isomerization of quadricyclane derivatives to the corresponding norbonadienes via various metal complexes.[13-18]



1a, **2a**, $R_1 = R_2 = H$; $\Delta H_{2a \to 1a} = -26\ kcal/mol$ [19]

1b, **2b**, $R_1 = R_2 = CO_2Me$; $\Delta H_{2b \to 1b} = -18.5\ kcal/mol$ [20]

Chart I



Since norbornadiene (**1a**) itself does not absorb sunlight (>300 nm), the research in this area has been directed toward the efficient photoisomerization of **1** to **2** under sunlight. Hitherto known approaches are divided into two categories: (i) the use of organic sensitizers,[21] polymers,

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Table I. Photochemical Isomerization of 1a to 2a in the Presence of Copper(I)-Nitrogen Ligand Catalysts[a]

Cu(I)	solvent	turnover no.[b]
$Ph_3PCuCl \cdot bpy$ (3)	THF	15
	CH_3CN	10
$Ph_3PCuCl \cdot phen$ (4)	EtOH	7
$Ph_3PCuCl \cdot phtha$ (5)	THF	8
	EtOH[c]	~17
$Ph_3PCuBr \cdot py$ (6)[d]	THF	3
CuCl	THF	0.4

[a] All irradiations were performed for 120 h by using a tungsten-halogen lamp (>320 nm); [1a] = 0.5 M, [Cu(I)] = 0.002 M. [b] Turnover number = (molar quantity of 2a after 120 h)/(molar quantity of catalyst). [c] See Experimental Section. [d] [1a] = 0.2 M.

or copper(I) catalysts,[7-12] which assist the photoisomerization of **1a** to **2a** under sunlight; (ii) photoisomerization[22-28] of norbornadiene derivatives substituted with an appropriate chromophore, e.g., dimethoxycarbonyl derivatives (**1b**).[1b,22] In spite of these improvements, the wavelength which can be utilized is limited to the shorter region. The sun's radiation spectra reaching the earth has a maximum in the visible region; hence the visible light is far stronger than the UV light. Consequently, one of the most important problems for the solar energy storage system is the efficient utilization of the longer wavelength region, that is, the low-energy light. We report our own approaches to this problem.[29]

Results and Discussion

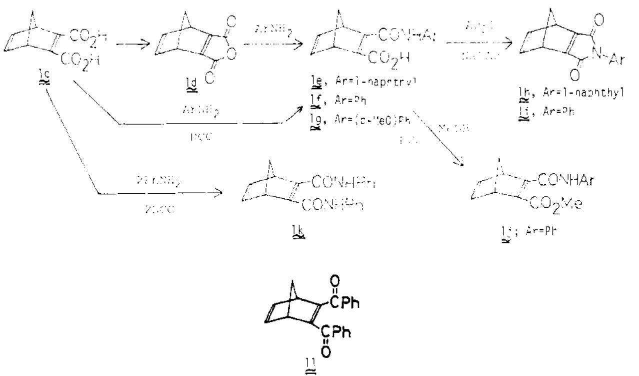
Photoisomerization of 1a to 2a with Copper(I)–Nitrogen Ligand Catalysts. It is well-known that copper(I) reacts with various nitrogen compounds such as pyridine and bipyridine to afford copper(I)–nitrogen ligand complexes.[30] These complexes normally exhibit a yellow or orange color, owing to the charge-transfer band between Cu and the ligand. We chose stable Ph_3PCuXL complexes[31] (X = Cl, Br; L = 2,2′-bipyridine, *o*-phenanthroline, phthalazine, etc., (Chart I). Compared with the CuCl–**1a** complex, (triphenylphosphine)copper(I)–nitrogen ligand complexes exhibit strong absorption in the near-UV region and a tail into the visible region. This fact suggests that the photoisomerization in the presence of these complexes may occur at longer wavelength light. This proved to be practical, and the results are summarized in Table I.

Any side reactions were not detected under normal reaction conditions. Prolonged irradiation gave higher turnover numbers, though slight decomposition of complexes was frequently encountered. As would be expected, use of CuCl catalyst under these conditions gave quite a disappointing result (turnover number of 0.4). It is noteworthy that complex **3** catalyzes the photoisomerization even in acetonitrile (Table I). Kutal and his coworkers report that CuCl does not catalyze the photoisomerization in acetonitrile, owing to the strong solvation which prevents the complex formation between CuCl and **1a**.[10] Therefore, it is suggested that the photoisomerization via **3** does not proceed through the complex formation between **3** and **1a**. Actually, examination of the UV spectra of norbornadiene–copper(I) complex systems indicates the absence of such a complex. Consequently, the reaction may proceed through the complex between the ground state **1a** and the excited Cu(I)* (eq 2). Kutal proposes a similar mechanism for $(Ph_3P)_2CuBH_4$.[11]

$$\mathrm{Cu(I)} \xrightarrow{h\nu} \mathrm{Cu(I)^*} \xrightarrow{\mathbf{1a}} [\mathrm{Cu(I)^*}\cdot\mathbf{1a}] \longrightarrow \mathbf{2a} + \mathrm{Cu(I)} \quad (2)$$

The efficiency of catalysts **3–5** is not so high, as is shown by the following quantum yields (Φ): **5**, Φ = 0.13 at 313 nm in EtOH and Φ = 0.011 at 366 nm in EtOH; **3**, Φ = 0.063 in THF at 313 nm and Φ ≃ 0.008 in THF at 366 nm; **4**, Φ = 0.032 in EtOH at 313 nm. Compared with the reported quantum yields of the photoisomerization via CuCl (0.23–0.42 at 313 nm),[10] those in our system are considerably lower. However, these catalysts can catalyze the photoisomerization at 366 nm, where the CuCl catalyst

Scheme I



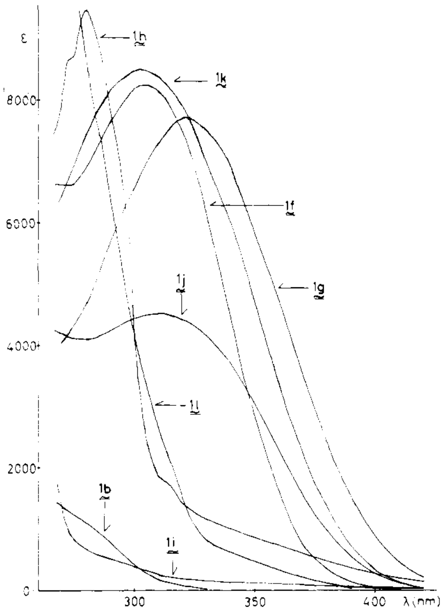


Figure 1. UV spectra of norbornadiene derivatives in acetonitrile as the solvent.

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Table II. Photoisomerization of Norbornadiene Derivatives to the Corresponding Quadricyclanes

norbornadiene	% yield of quadricyclane[a]	Φ [b]
1f	~100	0.09,[c] 0.088[d]
1g	~100	*e*
1h	78	0.12
1i	85	0.07[f]
1j	96	0.03
1k	92	0.02
1l	87	0.37
1b	100[g]	0.51[g,h]

[a] Determined by ^{1}H NMR spectra at 78-100% conversion, based on consumed 1. [b] Determined by ^{1}H NMR spectra at 366 nm. [c] Concentration of 1f is 1.5×10^{-2} M. [d] Determined by UV spectra. Concentration of 1f is 5.50×10^{-4} M. [e] Not determined. [f] At 313 nm. [g] Reference 22. [h] At 314 nm.

cannot induce the isomerization.

Other copper catalysts such as CuOTf, $[Ph_3PCuCl]_4$, and $(Ph_3P)_3CuBPh_4$ were also examined. However, these catalysts were not promising; CuCl exhibited a high turnover number. The reaction of CuCl in the presence of nitrogen ligands such as bipyridine and phthalazine without triphenylphosphine also proceeded similarly, but the efficiency was inferior to that of **3**–**6**, presumably due to the low stability of the catalyst.

Photoisomerization of Substituted Norbornadiene Derivatives. Although norbornadiene derivatives with relatively simple substituents are known to isomerize to the corresponding quadricyclanes photochemically, almost all of them do not absorb above 350 nm.[22-28] To solve this problem, we introduced arylcarbamoyl or arylimide groups to norbornadiene skeleton (Scheme I). UV spectra of norbornadiene derivatives **1b**, **f**–**l** are shown in Figure 1. Compounds **1f**–**l** have stronger absorption and a longer tail in the visible region than **1b**. Irradiation of an acetonitrile solution of **1f**–**l** in a Pyrex tube by using a high-pressure Hg lamp gave the corresponding quadricyclane derivatives in high yields. ^{1}H NMR, mass, and IR spectral and elemental analysis data of the photoproduct clearly indicated the quadricyclane structure. ^{1}H NMR spectra were especially helpful for the structure determination; the protons of the tetracyclic ring appeared at δ ($CDCl_3$) 2.0–3.2, indicating the saturated carbon framework. The pattern of the chemical shifts resembled quite well that of **1b** or other known quadricyclane derivatives. Furthermore, as mentioned later, the photoproduct underwent isomerization to the corresponding norbornadiene derivative with Rh(I) catalysts. Consequently, the structure of the photoproduct was unambiguously established.

Table II indicates the yields of photoisomerization determined from the ^{1}H NMR spectra. Although irradiation of **1h**,**j**,**k** was accompanied by the formation of small amounts of colored materials, an essentially quantitative isomerization was realized in the case of **1f** and **1g**. Therefore, **1f** and **1g** are promising as candidates for a solar energy storage system.[32] Furthermore, the isosbestic points at 229 and 274 nm clearly indicate the quantitative isomerization of **1f** (Figure 2).

Although irradiation of **1l** gave the corresponding quadricyclane,[33] the related compound, 1,4-dihydro-1,4-methanoanthraquinone (**1m**) did not afford the desired isomer. Since it is reported that irradiation of **1n** gives tarry materials,[34] and a similar complex reaction of may occur for **1m** (Chart II). Irradiation of **1e** also gave the corresponding quadricyclane in very low yield, and the investigation was not pursued further. The photochemical reaction of **1f** and **1i** in benzene afforded a result similar to that in acetonitrile, indicating that the solvent effect is not so important in these cases.

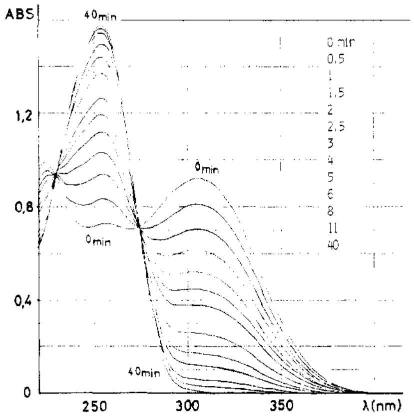
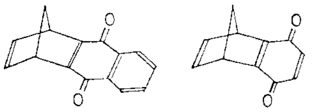


Figure 2. UV spectra of the photoisomerization of **1f** to **2f**. An acetonitrile solution of 1.13×10^{-4} M **1f** was irradiated with 313-nm light.

Chart II



1m **1n**

Table III. Photoisomerization of Norbornadiene Derivatives under Solar Irradiation[a]

norbornadiene	% conversion 7 h[b]	1 h[c]
1f	89	70
1b	71	59
1a	0	0

[a] An acetonitrile solution of 0.02 M of norbornadiene was irradiated in a pyrex tube in Kyoto. [b] For 7 h on Sept 29, a cloudy day. [c] For 1 h on Oct 9, a sunny day.

The quantum yield was measured at 313 or 366 nm, and the quantitative analysis of quadricyclane derivatives was performed with ^{1}H NMR (Table II). UV spectra[22] were also employed in the case of **1f**, and the identical quantum yield was obtained with both methods. This observation indicated that the quantum yield did not depend upon the concentrations under these reaction conditions. Unfortunately, relatively low quantum yields were obtained in comparison with that of **1b** (0.51);[22] Φ of **1f** $\simeq$ $^1/_6$(Φ of **1b**). However, irradiation under sunlight revealed that the isomerization of **1f** occured 1.2 times faster than that of **1b** (Table III). This is presumably due to the strong absorption of **1f** in near ultraviolet region.

Photostationary State for 1f and 2f. Apart from the solar energy storage system, the problem of the photostationary state of the norbornadien-quadricyclane system is very interesting.[25] The photostationary state was obtained by the irradiation of **1f** or **2f** at 254 nm. A mixture of **1f**/**2f** ratio of 9/1 was obtained irrespective of the starting material. On the assumption that $\epsilon_1[\mathbf{1f}]_{pss}\Phi_{1\rightarrow 2} = \epsilon_2[\mathbf{2f}]_{pss}\Phi_{2\rightarrow 1}$ and $\Phi_{1\rightarrow 2}/\Phi_{2\rightarrow 1} = 0.22$, this leads to $\Phi_{2\rightarrow 1} =$

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(32) Whether the photoisomerization of **1f** to **2f** proceeds in 100% yield or not is not obvious, since prolonged irradiation usually gives a slight amount of unknown yellow material.

(33) Recently, the reaction of **1l** was reported: Lahiri, S.; Dabral, V.; Chauhan, S. M. S.; Chakachery, E.; Kumar, C. V.; Scaiano, J. C.; George, M. V. *J. Org. Chem.* **1980**, *45*, 3782.

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0.4, when $\Phi_{1f\to2f}$ at 366 nm (0.09) is used because of lack of the data at 254 nm. Since **2f** does not absorb at a longer wavelength region than 310 nm (Figure 2), the irradiation under sunlight induced the isomerization in the desirable direction (**1f** → **2f**).

Pyrolysis of Quadricyclane Derivatives. The thermal stability of quadricyclane derivatives is also an important problem for the solar energy storage system. It is well-known that quadricyclane derivatives undergo thermal isomerization to the corresponding norbornadiene derivatives. For example, the half-life for **2a** → **1a** at 140 °C is 14 h, and that for **2b** → **1b** at 150 °C is 63 min.[20] Heating of **2f** and **2i** at 80 °C in benzene for 5 h resulted in the quantitative recovery of **2f** and in the slight isomerization (5%) of **2i** to **1i**. Heating of crystals of **2f,h–j** at 110 °C for 3 h resulted in essentially quantitative recovery of **2f** and **2j**, while it caused the isomerizatin of **2h** and **2i** into **1h** and **1i** in 50% yield. The half-life of **2h** and **2i** was about 3 h. The difference of thermal stability between the imides (**2h** and **2i**) and amides (**2f** and **2j**) may be ascribed to the steric strain arising from the five-membered cyclic structure of the imide derivatives. Most of **2f** and **2j** disappeared, and a complex mixture was obtained, when they were heated at 140 °C for 4 h. Among the mixture, the formation of **1f** (~30%) and **1i** (~10%) was observed.

Transition Metal Complex Catalyzed Back-Isomerization of 2 to 1. It is known that the isomerization of **2** to **1** is catalyzed by various metal complexes.[13-18] Although the reaction of **2a** is widely investigated, the information on the substituted quadricyclanes is not necessarily enough. Therefore, we first examined the reaction of **2b** with various metal catalysts. $Rh_2(CO)_4Cl_2$,[16] $Pd(PhCN)_2Cl_2$,[16] and $Ni(cod)_2$[17] acted as active catalysts as reported previously. $Pd_2(dba)_3CHCl_3$, $Pt(dba)_2$, and $RhCl(PPh_3)_3$ also exhibited high catalytic activity, while the activity of $Pd(PPh_3)_4$ and $Pd(cod)Cl_2$ was not so high. The isomerization was not detected with $Ru_3(CO)_{12}$, $Hg(OAc)_2$, $Pd_2Cl_4(PPh_3)_2$, and $Fe(CO)_5$. The catalytic activity toward **2f–i** was investigated by using $Rh_2(CO)_4Cl_2$, since it was stable and easy to handle. Hogeveen et al. reported that the isomerization of **2b** to **1b** via Rh(I) obeys Michaelis–Menten-type kinetics.[16] The isomerization of **2f–i** via $Rh_2(CO)_4Cl_2$ proceeded similarly in an essentially quantitative yield. Apparent second-order rate constants for the initial stage of the isomerization at 35 °C, which are obtained by ^{1}H NMR spectra, are summarized in Table IV. The rate of **2a** at 35 °C was calculated from the reported data[15] at −26 °C by assuming log $A = 7$ in the Arrenius equation.[35] Owing to the low solubility of **2f** in $CDCl_3$, the experiment was carried out with a substrate concentration of 0.1 M in acetone-d_6. The rates for **2f,h–j** were almost the same order of magnitude as that of **2b** and were almost 10^2 times lower than that of **2a**. It is well-known that the isomerization rate of small-ring compounds via Rh(I) decreases by about 10^2 times when they are substituted with carbonyl groups.[35] Therefore, the present observation for **2f,h–j** is presumably a reflection of the carbonyl substituent.

Experimental Section

Apparatus. All melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. Infrared spectra were measured with a JASCO IRA-1 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL JNM-MH-100 instrument; chemical shifts (δ) are expressed in parts per million relative to tetramethylsilane. The ultraviolet and visible spectra were measured with a Shimadzu UV-200 spectrometer. VPC analysis was carried out with a Shimadzu GC-4CM gas chromatograph containing a 2 m × 3 mm 25% silicon DC-550 on Celite 545 (60–80 mesh) glass column. For a quantitative analysis of nonsubstituted quadricyclane, the injection temperature was set at 100 °C, and the column temperature was kept below 100 °C. The elemental analyses were performed at the Microanalysis Center of Kyoto University.

Table IV. Rh(I)-Catalyzed Isomerization of Quadricyclane Derivatives to the Corresponding Norbornadienes

quadricyclane	k,[a] M^{-1} s^{-1}	rel rate
2f	1.6×10^{-2} [b]	0.94
2h	1.5×10^{-2}	0.88
2i	9.2×10^{-3}	0.54
2j	1.4×10^{-2}	0.82
2b	1.7×10^{-2}	1
2a	5.5×10^{-2} [c]	~10^2 [d]

[a] Initial rate constant; $v_0 = k[Rh]_0[\mathbf{2}]_0$. This is not a real second-order rate constant. $[Rh_2(CO)_4Cl_2]_0 = 0.01$ M and $[\mathbf{2}]_0 = 0.2$ M, in $CDCl_3$. [b] $[\mathbf{2f}]_0 = 0.1$ M, in acetone-d_6. [c] Reference 15. At −26 °C, $[\mathbf{2a}]_0 = 0.6$ M and $[Rh_2(NBD)_2Cl_2] = 0.03$ M. [d] Extrapolated value, on the assumption that log $A = 7$. See ref 35.

Materials. Commercially available norbornadiene was distilled from sodium under an argon atmosphere. All solvents for photolysis were dried by standard techniques and distilled under argon or nitrogen. For other purposes reagent grade solvents were simply distilled except as otherwise noted. All copper(I) catalysts[30] except **5** (vida infra) and metal catalysts for back-isomerization were synthesized according to the literature procedures. n-Octane, pentachloroethane, and 1,1,2,2-tetrachloroethane (as internal standards for VPC and NMR quantitative analyses) were commerically available and used without further purification. Quadricyclane (**2a**),[18b] 2,3-dibenzoylnorbornadiene (**1l**),[36] **1m**,[37] norbornadiene-2,3-dicarboxylic acid (**1c**),[38] its anhydride (**1d**),[27] dimethylnorbornadiene-2,3-dicarboxylate (**1b**),[38] and dimethyl quadricyclane-2,3-dicarboxylate (**2b**)[22] were synthesized by the literature procedures.

Synthesis of PPh_3CuCl·phtha (5). Compound **5** was synthesized in a simmilar manner to that for **3**. $[CuClPPh_3]_4$ (0.72 g, 0.50 mmol) and commercially available phthalazine (0.26 g, 2.0 mmol) were stirred overnight in dry ether (50 mL). Yellow precipitates were formed. Filtration, washing with ether, and drying in vacuo gave the desired complex in nearly quantitative yield: mp 196–199 °C dec. Anal. Calcd for $C_{26}H_{21}N_2PClCu$: C, 63.55; H, 4.31; N, 5.70. Found: C, 62.93; H, 4.19; N, 5.12.

Photoisomerization of 1a Catalyzed by Copper(I)–Nitrogen Ligand Complexes. General Procedure. Norbornadiene (15 mmol) and n-octane (6 mmol) were added to a solution of Ph_3PCuXL complex (0.06 mmol) in an appropriate solvent. When the complex was difficult to dissolve at room temperature, the mixture was warmed slightly. Solvent was added until the total volume reached 30 mL. The solution (5 mL) was transfered to an argon-purged hard-glass tube via a syringe and irradiated with a 300-W tungsten–halogen lamp (Ushio JCV-100-300W) for 120 h. VPC analysis was carried out by using n-octane as an internal standard.

The solubility of **5** in ethanol at room temperature was quite low. On being warmed, the solution turned pale yellow, and small amounts of white precipitates appeared. Since this supernatant liquid was used, the exact concentration of copper(I) must be lower than 0.002 M.

THF solution of CuCl–**1a** was prepared according to the literature procedure.[10]

Quantum Yields of Isomerization of 1a Catalyzed by Copper(I)–Nitrogen Ligand Complexes. A super-high-pressure mercury projector lamp (500-W) was used as a light source. A combination of a Corning 7-54 glass filter and $NiSO_4$(aq) and

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K_2CrO_4(aq) solution filters was used for isolation of 313-nm light.[39] A combination of a Corning 7-37 glass filter and $CuSO_4$(aq) and 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate solution filters was used for isolation of 366-nm light.[39] A mixture of 0.50 M norbornadiene, (1–4) × 10^{-3} M *n*-octane, and 2.0 × 10^{-3} M catalyst (except for **5**) in ethanol (vide supra) was irradiated under argon.

Photoisomerization of 1a Catalyzed by Certain Copper(I) Complexes. $(Ph_3P)_3CuBPh_4$ (117 mg, 0.100 mmol) was dissolved in THF (ca. 17 mL) in a Pyrex tube, and then argon was bubbled in for several minutes. Norbornadiene (924 mg, 10.0 mmol) and *n*-octane (440 mg, 3.85 mmol) were added under an argon atmosphere, and then THF was added until the total volume of the solution reached 20 mL. The Pyrex tube was tightly sealed with a rubber cap and irradiated with a 300-W high-pressure mercury lamp for 60 h. VPC examination revealed that 80% of norbornadiene was recovered and 8% of quadricyclane was formed. The turnover number was calculated as 8.

A similar procedure was used for $[Ph_3PCuCl]_4$, which was weighed on the basis of the monomer "Ph_3PCuCl", and for $CuCl{\cdot}SMe_2$, which was dissolved in a mixed solvent of MeSMe (40% v/v) and ether. In the case of the former, 80% norbornadiene was recovered, and 20% of quadricyclane (turnover number 20) was formed after 60 h of irradiation. In the case of the latter, 44% of norbornadiene was recovered, and 12% of quadricyclane (turnover number 12) was formed after 9 days of irradiation.

An ether solution (0.1 M, 1 mL) of $CuOTf{\cdot}0.5C_6H_6$, which was extremely air sensitive, was syringed carefully into a Pyrex tube under argon. Norbornadiene, *n*-octane, and ether were added as described before, and then the solution was irradiated for 60 h similarly. VPC analysis showed the recovery of 75% of norbornadiene and the formation of 25% of quadricyclane (turnover number 25).

For CuCl-**1a**, 69% of norbornadiene was recovered, and 31% of quadricyclane (turnover number 31) was formed after 60 h of irradiation.

Photoisomerization of 1a Catalyzed by CuCl in the Presence of Nitrogen Compounds. Guaranteed grade CuCl (25 mg, ca. 0.25 mmol), 2,2′-bipyridine (39 mg, 0.25 mmol) or phthalazine (32.5 mg, 0.25 mmol), THF (47 mL), *n*-octane (1.06 g, 9.28 mmol), and norbornadiene (2.30 g, 25 mmol) were stirred for 1 h under argon. The red solution of bipyridine contained small amounts of red precipitates. The yellow solution of phthalazine also contained small amounts of yellow precipitates. The precise concentration of copper(I) in solution was not obvious. The supernatant solution was irradiated and analyzed as described; quadricyclane was formed in 2% and 6% yields, respectively. The remainder was unreacted norbornadiene.

Synthesis of 3-(Phenylcarbamoyl)norbornadiene-2-carboxylic Acid (1f). The procedure for the synthesis of maleic acid monoanilide from maleic anhydride and aniline was empolyed.[40] **1d** (6.97 g, 43.0mmol) was dissolved in dichloromethane (100 mL) at 0 °C. Dichloromethane (30 mL) solution of freshly distilled aniline (4.00 g, 43.0 mmol) was added dropwise at 0 °C. After the solution was stirred for 1 h at 0 °C under nitrogen, the solvent was evaporated. Ether was addd and the mixture kept in a refrigerator. Filtration of the resulting yellow crystals followed by washing with ether gave substantially pure **1f**: 10.26 g (93%). Recrystallization from dichloromethane and ether gave analytically pure crystals (slightly yellow): mp 151–152 °C dec; IR (KBr) 3000–3600 (br, CO_2H), 3300 (NH), 1690 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.08–2.50 (m, 2 H), 4.25 (m, 2 H), 6.98 (m, 2 H), 7.2–7.8 (m, 5 H), 9.17 (br, 1 H), 12.6–13.7 (br, 1 H); mass spectrum, *m/e* (relative intensity) 255 (M^+, 8), 93 (100). Anal. Calcd for $C_{15}H_{13}O_3N$: C, 70.56; H, 5.13; N, 5.49. Found: C, 70.29; H, 4.95; N, 5.23.

Synthesis of 3-(1-Naphthylcarbamoyl)norbornadiene-2-carboxylic Acid (1e). Use of commercially available 1-naphthylamine (Merck) instead of aniline gave **1e**: 88% yield; mp (from acetone–ether) 184–187 °C dec; IR (KBr) 3300–2600 (br, CO_2H, NH), 1670 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.96–2.30 (m, 2 H), 4.11 (m, 1 H), 4.22 (m, 1H), 6.88 (m, 2 H), 7.3–8.0 (m, 7 H), 9.77 (br, 1 H), 10.4–11.5 (br, 1 H); mass spectrum, *m/e* (relative intensity) 305 (M^+, 20), 260 (50), 143 (100), 66 (75). Anal. Calcd for $C_{19}H_{15}NO_3$: C, 74.74; H, 4.95; N, 4.59. Found: C, 75.00; H, 4.86; N, 4.34.

Synthesis of 1f. Compound **1f** was also synthesized from **1c** and aniline directly with DCC (dicyclohexylcarbodiimide) as a dehydration reagent. **1c** (2.70 g, 15.0 mmol) was dissolved in dry acetone (50 mL). Aniline (1.22 g, 15.0 mmol) was added, and then a dry acetone solution (15 mL) of DCC (3.09 g, 15.0 mmol) was added dropwise. White precipitates of dicyclohexylurea were formed during the addition. The mixture was stirred overnight at room temperature. Filtration, concentration in vacuo, and the addition of benzene or ether led to slightly yellow crystals. Simple filtration gave **1f** in 58% yield. From the mother liquor was obtained more **1f** (total yield 75%). Compound **1f** thus obtained exhibited a melting point similar to that previously described.

Synthesis of 3-[(*p*-Methoxyphenyl)carbamoyl]norbornadiene-2-carboxylic Acid (1g). Similar reaction of **1c** with anisidine gave **1g** in 76% yield; yellow prisms from acetonitrile–benzene: mp 179–180 °C; IR (KBr) 2800–3400 (br, CO_2H), 3260 (NH), 1675 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.1–2.4 (m, 2 H), 3.82 (s, 3 H), 4.08 (m, 2 H), 6.8–7.0 (m, 2 H), 6.96 (m, 2 H), 7.4–7.6 (m, 2 H), 8.44 (br, 1 H), 10.7 (br, 1 H); mass spectrum, *m/e* (relative intensity) 285 (M^+, 15), 124 (100), 108 (40), 66 (30). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.44; H, 5.56; N, 4.85.

Synthesis of *N*-Phenylnorbornadiene-2,3-dicarboximide (1i). A mixture of **1f** (5.11 g, 20.0 mmol), dry sodium acetate (1.0 g, 12 mmol), and freshly distilled acetic anhydride (30 mL) was heated to 100 °C for 1 h under a nitrogen atmosphere. The reaction mixture was concentrated in vacuo (1–2 torr). Aqueous sodium bicarbonate (ca. 25 mL) was added, and stirring was continued for 1 h at room temperature. Extraction with dichloromethane, washing with aqueous sodium bicarbonate and water, drying over anhydrous sodium sulfate, and concentration gave a heavy liquid, which was chromatographed on silica gel (Wakogel C-200) with benzene as the eluant. From the first-eluted yellow band was obtained **1i** as pale yellow crystals: 19% yield (0.90 g); mp 119–121 °C dec (from benzene–petroleum ether); IR (KBr) 1760 (C=O), 1705 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.62 (m, 2 H), 4.02 (m, 2 H), 6.90 (m, 2 H), 7.2–7.6 (m, 5 H); mass spectrum, *m/e* (relative intensity) 237 (M^+, 70), 143 (60), 118 (60), 90 (100). Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90. Found: C, 75.89; H, 4.87; N, 5.90. **1i** underwent slow oxidation with air.

Synthesis of *N*-(1-Naphthyl)norbornadiene-2,3-dicarboximide (1h). A similar reaction of **1e** with sodium acetate and acetic anhydride gave **1h**, which also underwent slow air oxidation: 17% yield; yellow crystals; mp 180–182 °C dec (from benzene–petroleum ether); IR (KBr) 1760 (C=O), 1700 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.66 (m, 2 H), 4.07 (m, 2 H), 7.00 (m, 2 H), 7.2–8.0 (m, 7 H); mass spectrum, *m/e* (relative intensity) 287 (M^+, 100), 169 (10), 118 (31), 90 (100). Anal. Calcd for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56, N, 4.88. Found: C, 79.73; H, 4.82; N, 4.72.

Synthesis of Methyl 3-(Phenylcarbamoyl)norbornadiene-2-carboxylate (1j). To a mixture of methanol (0.25 mL, ca. 6 mmol), dichloromethane (30 mL), and **1f** (1.20 g, 4.70 mmol) was added slowly a dichloromethane solution (4 mL) of DCC (0.97 g, 4.7 mmol). After being stirred overnight at room temperature, the mixture was concentrated, with the total volume reaching about 10 mL. The filtrate was chromatographed with benzene as an eluant. From the first-eluted pale yellow band was obtained **1j** as a pale yellow viscous oil: 66% yield; IR (neat) 3250 (NH), 1685 (C=O), 1660 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.96–2.26 (m, 2 H), 3.85 (s, 3 H), 4.10 (m, 1 H), 4.36 (m, 1 H), 6.90 (m, 2 H), 7.0–7.4 (m, 3 H), 7.6–7.8 (m, 2 H); mass spectrum, *m/e* (relative intensity) 269 (M^+, 20), 149 (100). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.19. Found: C, 71.10; H, 5.50; N, 5.19.

Synthesis of Norbornadiene-2,3-dicarboxanilide (1k). Compound **1k** was obtained through the reaction of **1c** with aniline (2 equiv) in the presence of DCC (2 equiv) in dry acetone. A similar workup and chromatography with dichloromethane as an

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eluant gave pale yellow prisms in 93% yield. Recrystallization from hot benzene gave an analytically pure sample: mp 195–196.5 °C; IR (KBr) 3280 (br, NH), 1650 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.0–2.3 (m, 2 H), 4.18 (m, 2 H), 6.96 (m, 2 H), 7.0–7.4 (m, 3 H), 7.5–7.7 (m, 2 H), 9.86 (br, 2 H); mass spectrum, *m/e* (relative intensity) 330 (M^+, 1), 93 (100), 66 (15). Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.52; H, 5.48; N, 8.19.

General Procedure for the Synthesis of Quadricyclane Derivatives. An acetonitrile solution [(1.0–2.0) × 10^{-2} M] of norbornadiene derivatives was prepared under an argon or nitrogen atmosphere in Pyrex tubes and was irradiated with a 300-W high-pressure mercury lamp for 5–20 h. For irradiation of **1g**, a filter solution of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate[39] was used in order to cut off light not profitable for photochemical reaction of **2g**. For preparation of **2f** and **2g**, the irradiated solution was directly evaporated to dryness to give reasonably pure **2f** and **2g**. For other compounds, the reaction mixtures were chromatographed over silica gel with benzene and/or dichloromethane as an eluant.

3-(Phenylcarbamoyl)quadricyclane-2-carboxylic Acid (2f): white crystals; ~100% yield; mp 156–158 °C dec (from benzene or dichloromethane); IR (KBr) 3300–2600 (br, CO_2H, NH), 1650 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.1–2.9 (m, 6 H), 7.0–7.7 (m, 5 H), 8.8–9.4 (br, 1 H), 10.7–11.0 (br, 1 H); mass spectrum, *m/e* (relative intensity) 255 (M^+, 10), 210 (35), 93 (100), 66 (35).

3-[(*p*-Methoxyphenyl)carbamoyl]quadricyclane-2-carboxylic Acid (2g): white crystals; ~100% yield; mp (from acetonitrile) 180–182 °C; IR (KBr) 3400 (NH), 3300–2700 (br, CO_2H), 1670 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.06–2.84 (m, 6 H), 3.75 (s, 3 H), 6.7–6.9 (m, 2 H), 7.3–7.5 (m, 2 H), 9.7–10.3 (br, 1 H), 10.70 (br, 1 H); mass spectrum, *m/e* (relative intensity) 285 (M^+, 15), 124 (100), 108 (55), 69 (60), 66 (50).

***N*-Phenylquadricyclane-2,3-dicarboximide (2i)**: white crystals; isolated yield 73% (based on consumed **1i**); mp 155–156 °C (from benzene–dichloromethane); IR (KBr) 1765 (C=O), 1705 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.27–2.66 (m, 2 H), 2.75–3.10 (m, 4 H), 7.2–7.7 (m, 5 H); mass spectrum, *m/e* (relative intensity) 237 (M^+, 40), 93 (100), 66 (25). Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90. Found: C, 75.84; H, 4.43; N, 5.81.

***N*-(1-Naphthyl)quadricyclane-2,3-dicarboximide (2h)**: white crystals; isolated yield 76% (based on consumed **1h**); mp 173–174 °C dec (from benzene–dichloromethane); IR (KBr) 1755 (C=O), 1700 cm^{-1} (C =O); ^1H NMR ($CDCl_3$) δ 2.26–2.68 (m, 2 H), 2.8–3.2 (m, 4 H), 7.3–8.1 (m, 7 H); mass spectrum, *m/e* (relative intensity 269 (M^+, 15), 90 (100). Anal. Calcd for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.87. Found: C, 79.45; H, 4.38; N, 4.76.

Methyl 3-(Phenylcarbamoyl)quadricyclane-2-carboxylate (2j): white crystals; isolated yield 89%; mp 84–85 °C (from benzene–petroleum ether); IR (KBr) 3300 (NH), 1670 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.04–2.74 (m, 6 H), 3.64 (s, 3 H), 6.95–7.38 (m, 3 H), 7.50–7.70 (m, 2 H), 11.2 (br, 1 H); mass spectrum, *m/e* (relative intensity) 269 (M^+, 4), 149 (100), 93 (50), 56 (55). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.36; H, 5.56; N, 5.18.

Quadricyclane-2,3-dicarboxanilide (2k): white crystals; isolated yield 84%; mp 181–182 °C (partial dec) (from hot benzene); IR (KBr) 3280 (br, NH), 1650 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.0–2.6 (m, 6 H), 7.0–7.8 (m, 10 H), 9.86 (br, 2 H); mass spectrum, *m/e* (relative intensity) 330 (M^+, 2), 93 (100), 66 (17). Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.15; H, 5.79; N, 8.41.

Determination of Chemical Yields. An acetonitrile solution [(1–2) × 10^{-2} M] of norbornadiene derivatives in argon filled Pyrex tubes was irradiated as described before. Chemical yields of norbornadiene derivatives recovered and quadricyclane derivatives were determined by ^1H NMR using pentachloroethane as an internal standard. Reaction conditions and the results are summarized in Table V.

Determination of Isobestic Points in UV Spectra on Photoisomerization of 1f. An acetonitrile solution (1.13 × 10^{-4} M) of **1f** in an Ar-filled UV cell was irradiated with 313-nm filtered light. After an appropriate time interval the cell was transfered into the UV spectrometer and the spectrum was recorded.

Quantum Yields of Isomerization of Norbornadiene Derivatives. An apparatus and actinometer similar to those described previously were used. Samples were prepared under an argon atmosphere, and the concentrations of norbornadiene derivatives in acetonitrile were as follows: **1f**, 0.015 M; **1h**, 0.01 M; **1i**, 0.02 M; **1j**, 0.01 M; **1k** 0.015 M; **1l**, 0.025 M. Irradiation of **1h–l** was stopped before the conversion reached 10%, because higher conversion gave some colored materials. The yield of quadricyclane derivatives was determined by ^1H NMR with pentachloroethane as an internal standard. An average value from two or three experiments is indicated as the quantum yield.

Table V. Determination of Chemical Yield

compd	[1], M	irradiation time, h	% recovery of 1	% yield of 2[a]
1f	0.01	10	~0	~100
1g	0.01	15	~0	~100
1h	0.01	10	23	60
1i	0.01	10	9	77
1j	0.02	6.5	~0	96
1k	0.01	10	~0	92
1l	0.015	5	23	67

[a] Based on the amount of 1 used.

Photoisomerization by Sunlight. Respective acetonitrile solutions of 0.02 M of **1a,b,f** in argon-filled sealed tubes were irradiated for 7 h on Sept 29, a cloudy day, from 11:00 a.m. to 6:00 p.m. in Kyoto, Japan. Quite similar irradiations were performed for 1 h on Oct 9, a sunny day, PM from 12:00–1:00 p.m. in Kyoto, Japan. Yields of quadricyclane derivatives were determined by ^1H NMR and VPC.

Photostationary State of 1f and 2f. An acetonitrile solution (1.61 × 10^{-4} M) of **1f** was irradiated with 254-nm light from a low-pressure mercury lamp, isolated by means of $NiSO_4$(aq) and 2,7-dimethyl-3,6-diaza-cyclohepta-1,6-diene perchlorate solution filters.[38] Irradiation for 30 min gave the photostationary mixture of **1f** and **2f**. It was revealed that [**1f**]/[**2f**] = 90:10 from the absorbance at 254 nm by use of their molar extinction coefficients at 254 nm (ϵ_{1f} 6440, ϵ_{2f} 13900). This ratio did not change even after 90 min.[31] An acetonitrile solution (8.34 × 10^{-5} M) of **2f** was irradiated similarly. Here again, the photostationary state was obtained; [**1f**]/[**2f**] = 91:9.

Pyrolysis of Quadricyclane Derivatives. An oil bath equipped with a thermoregulator was used for heating. Fluctuation of temperature was ±2 °C. In pyrolysis at 80 °C, solutions (0.06–0.08 M) of quadricyclane derivatives in dry benzene were used. Pyrolysis of **2i** at 80 °C for 5 h gave 5% of **1i** along with recovery of **2i** (95%). Pyrolysis at 110 and 140 °C was carried out without solvent. Yields were determined by ^1H NMR as described before.

Check of Catalytic Activity of Various Metal Complexes for Isomerization of 2b. About 50 mg of **2b** was mixed with solvent (1 mL) and catalytic amounts of metal complexes. In the cases of $Pd(PPh)_4$ and $Ni(cod)_2$, the preparation was performed under argon. After the mixtures were allowed to stand overnight or 3 days, TLC and/or ^1H NMR analysis was carried out. Metal complexes and solvents used were as follows: (i) $Ni(cod)_2$, toluene, acetone; (ii) $Pd_2(dba)_3CHCl_3$, $CHCl_3$; (iii) $Pt(dba)_2$, $CHCl_3$; (iv) $RhCl(PPh_3)_3$, $CHCl_3$; (v) $PdCl_2(cod)$, $CHCl_3$, acetone; (vi) $Ru_3(CO)_{12}$, hexane; (vii) $Hg(OAc)_2$, MeOH–$CHCl_3$; (viii) $Pd_2Cl_4(PPh_3)_2$, $CHCl_3$, benzene; (ix) $Rh_2(CO)_4Cl_2$, $CHCl_3$, acetone; (x) $Pd(PPh_3)_4$, acetone; (xi) $Fe(CO)_5$, benzene.

$Rh_2(CO)_4Cl_2$-Catalyzed Back-Isomerization of Quadricyclane Derivatives. A $CDCl_3$ solution of quadricyclane derivatives and pentachloroethane in an NMR sample tube was warmed at 35 °C. A $CDCl_3$ solution of $Rh_2(CO)_4Cl_2$, which was also preheated up to 35 °C, was added to the solution, and more $CDCl_3$ was added so that the concentration of quadricyclane derivatives and $Rh_2(CO)_4Cl_2$ were 0.2 and 0.01 M, respectively. The sample tube was put into an NMR probe quickly, which was also set at 35 °C in advance. Signals of norbornadienes, quadricyclanes, and pentachloroethane were integrated at an appropriate time interval. Molar quantities of norbornadienes and quadricyclanes were calculated and plotted vs. time. The initial apparent rate constant was determined from initial slope of the curve thus obtained. The rate constant determined is based on the average value of at least two measurements.

For **2f**, 0.1 M acetone-d_6 solution and 1,1,2,2-tetrachloroethane as an internal standard were used.

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Registry No. 1a, 121-46-0; **1b**, 947-57-9; **1c**, 15872-28-3; **1d**, 826-62-0; **1e**, 79632-14-7; **1f**, 78941-78-3; **1g**, 79632-15-8; **1h**, 79632-16-9; **1i**, 79632-17-0; **1j**, 79632-18-1; **1k**, 79632-19-2; **2a**, 278-06-8; **2b**, 714-53-4; **2f**, 78941-77-2; **2g**, 79632-20-5; **2h**, 79632-21-6; **2i**, 79632-22-7; **2j**, 79632-23-8; **2k**, 79632-24-9; **3**, 25753-80-4; **4**, 14751-81-6; **5**, 79647-68-0; **6**, 25753-77-9; $(Ph_3P)_3CuBPh_4$, 34013-06-4; $[Ph_3PCuCl]_4$, 25895-58-3; CuOTf, 25535-55-1; $Rh_2(CO)_4Cl_2$, 14523-22-9; CuCl, 7758-89-6; aniline, 62-53-3; 1-naphthylamine, 134-32-7; *p*-anisidine, 104-94-9.

Photostimulated Reactions of Alkanethiolate Ions with Haloarenes. Electron Transfer vs. Fragmentation of the Radical Anion Intermediate[1]

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The photostimulated reactions of RS^- ions (R = methyl, *n*-butyl, *tert*-butyl, and benzyl) with haloarenes in liquid ammonia were studied. Two main products were formed: alkyl aryl sulfide and arenethiolate ions. The formation of these compounds is explained by the $S_{RN}1$ mechanism of aromatic nucleophilic substitution. The radical anion intermediate formed in the coupling of an aryl radical with an alkanethiolate ion undergoes two competing reactions: transfer of the odd electron to the substrate leading to the substitution product or bond fragmentation leading to arenethiolate ion and an alkyl radical. It is concluded that the ratio of these products depends mainly on changes in the rate of fragmentation and not on changes in the electron-transfer reaction.

The photostimulated reaction of iodobenzene (**1**) with benzenethiolate ion (**2**) in liquid ammonia has been shown to give diphenyl sulfide (**3**) in nearly quantitative yield by $S_{RN}1$ mechanism of aromatic nucleophilic substitution (eq 1).[2] The photostimulated reaction of **1** with ethanethiolate

$$\underset{\mathbf{1}}{PhI} + \underset{\mathbf{2}}{PhS^-} \xrightarrow{h\nu} \underset{\mathbf{3}}{PhSPh} + I^- \qquad (1)$$

ion (**4**) is much slower, releasing only 60% of the theoretical amount of iodide ion after 90 min of irradiation. When this reaction is carried out for 200 min and then quenched with benzyl chloride, the products are phenyl ethyl sulfide (**8**, 30%), phenyl benzyl sulfide (**10**, 44%), and diphenyl sulfide (**3**, 3%). These results were interpreted by the $S_{RN}1$ mechanism shown in Scheme I.[3-5]

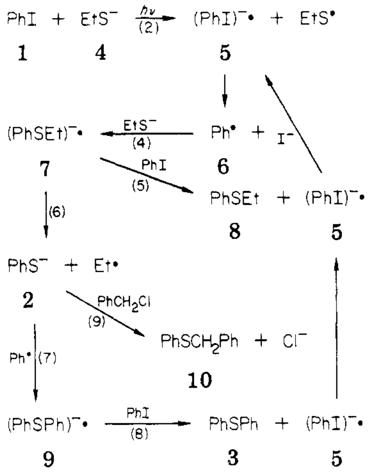
The principal course of the chain reaction is by eq 5 (in Scheme I). The formation of ethyl radical in eq 6 is a chain-terminating step, which depresses the overall reaction. The reaction of **2** to give **3** via eq 7 and 8 is minor, but the presence of **2** is shown by trapping with benzyl chloride to give **10** (eq 9).

The photostimulated reaction of the sodium salts of *n*-butanethiolate and 2-hydroxyethanethiolate ions with 1-chloro- or 1-bromonaphthalene in liquid ammonia has been shown to give naphthalene and the alkyl naphthyl sulfides in good yields without any product derived from fragmentation of the radical anion intermediate formed in the sense of eq 6.[6]

$$C_{10}H_7X + RS^- \xrightarrow{h\nu} C_{10}H_7SR + X^-$$
$$X = Cl, Br; R = n\text{-Bu}, OHCH_2CH_2$$

In the electrochemically induced $S_{RN}1$ reaction of 4-bromobenzophenone with PhS^-, CH_3S^-, or t-BuS^- ions in $(Me)_2SO$ or acetonitrile, the only products reported were benzophenone and the 4-benzoylphenyl sulfides resulting from substitution; no products resulting from bond fragmentation were obtained.[7]

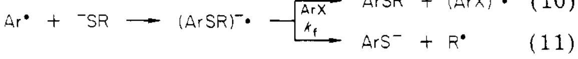
Scheme I



The contrasting behavior of iodobenzene compared with 1-halonaphthalenes and 4-bromobenzophenone in the reaction with RS^- ions prompted us to investigate the reactions of several aryl halides with alkanethiolate ions to determine the factors that affect the balance between the electron-transfer reaction (eq 10) and bond fragmentation (eq 11) of the aryl alkyl sulfide radical ion intermediates.

Results

Equations 4–6 in Scheme I can be generalized as shown in eq 10 and 11, where k_t and k_f are rate constants for the



$$Ar^\bullet + {}^-SR \longrightarrow (ArSR)^{-\bullet} \begin{cases} \xrightarrow[ArX]{k_t} ArSR + (ArX)^{-\bullet} & (10) \\ \xrightarrow{k_f} ArS^- + R^\bullet & (11) \end{cases}$$

electron transfer and the bond fragmentation reactions,

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