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Reactivities of Stable Rotamers. XLII. Generation and Fates of Rotameric [1-(9-Fluorenyl)-2-naphthyl]methyl Radicals1)

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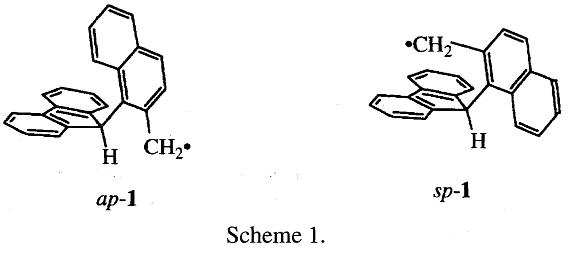
The title radical rotamers were generated by thermolyses of the corresponding *t*-butyl peroxycarboxylates or photolyses of the corresponding 2(1*H*)-thioxo-1-pyridyl carboxylates. Products from the *t*-butyl peroxyesters were *t*-butoxy compounds, dimers, and colligation products with a benzyl radical, when the reactions were carried out in toluene. In carbon tetrachloride, chlorine-abstraction products and colligation products with a trichloromethyl radical were obtained in addition to the dimers. Photolyses of the 2(1*H*)-thioxo-1-pyridyl esters afforded expected products, the dimers and 2-pyridylthio derivatives. Generally, the differences from one rotamer to another cause minor differences in the distribution of the products. The small differences are attributed to the steric effects which operate at the site where the radical is produced.

The behaviors of diastereomeric rotational isomers are different from each other in many reactions.[2] The differences are sometimes negligibly small, but in other cases they are surprisingly large. Radical reactions of rotamers are no exception. We have shown that the products from radical reactions of rotamers of triptycene series are affected by substituents which are in close proximity to the radical center.[3,4] These results encouraged us to examine radical reactions of rotamers of 9-arylfluorenes, which comprise another series of stable rotamers at room temperature. We wish to report the results of the study on the products derived from [1-(9-fluorenyl)-2-naphthyl]methyl radicals (**1**) (Scheme 1) in this paper.

The starting materials for the generation of the radicals were synthesized in the following ways (Scheme 2). *sp*-1-(9-Fluorenyl)naphthalene-2-carboxylic acid (*sp*-**2**) was converted to the acid chloride and then treated under the Arndt–Eistert reaction[5] conditions to produce methyl *ap*-[1-(9-fluorenyl)-2-naphthyl]acetate (*ap*-**3**). The formation of the acid chloride from *sp*-**2** was slow, but satisfactory yields were obtained when the prolonged reaction time was allowed. *ap*-**3** was heated in toluene to isomerize and the resulted mixture was separated by chromatography to yield *ap*-**3** and *sp*-**3**. Compound **3** was hydrolyzed to produce the corresponding carboxylic acid (**4**), which was converted to *t*-butyl [1-(9-fluorenyl)-2-naphthyl]peracetate (**5**) by treatment of the acid chloride with *t*-butyl hydroperoxide. The corresponding 2(1*H*)-thioxopyridyl esters (**6**) were prepared similarly by treatment of the acid chloride with the sodium salt of 2-mercaptopyridine 1-oxide (Scheme 3).



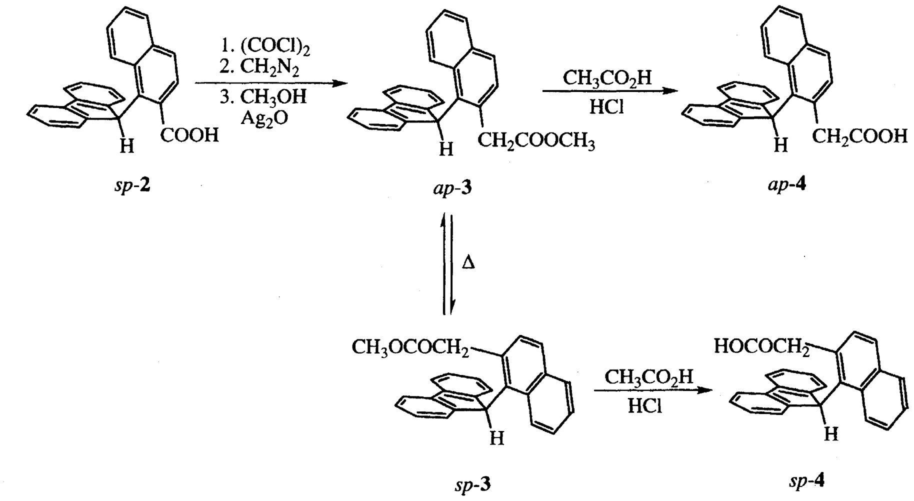
ap-**1** *sp*-**1**

Scheme 1.

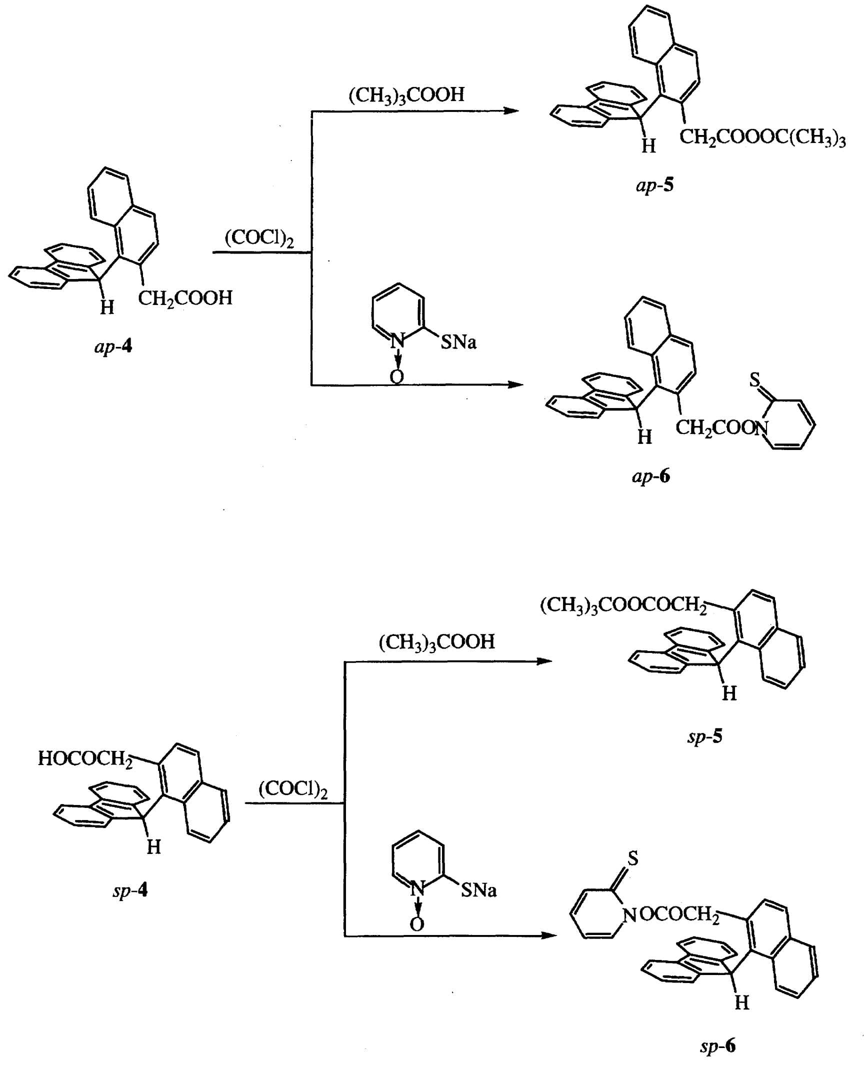
The *t*-butyl esters were thermolyzed at 80 °C or lower temperatures and the thioxopyridyl esters were photolyzed at room temperature. These conditions had to be used because of the rather facile isomerization of these rotamers.

Thermolyses of Compounds 5. In Toluene. In toluene, they afforded 1-(9-fluorenyl)-2-(*t*-butoxymethyl)naphthalene (**7**), 1,2-bis[1-(9-fluorenyl)-2-naphthyl]ethane (**8**) and 1-(9-fluorenyl)-2-(2-phenylethyl)naphthalene (**9**) (Scheme 4). The yields of these products normalized to 100% are shown in Table 1 and actual ones in the Experimental section. The decomposition was a little faster for *ap*-**5** than for *sp*-**5**, as evidenced by the fact that, under the same conditions, 9% *sp*-**5** remained unreacted, whereas *ap*-**5** was decomposed completely (See Experimental). The identification of the products was carried out by either an independent synthesis or by ^{1}H NMR spectroscopy together with elemental analyses.

Since there is no report in the literature that mentions thermolyses of *t*-butyl naphthaleneperacetate, we may compare the results with those of *t*-butyl phenylperacetate. In the literature, most of the investigators seem to be interested in

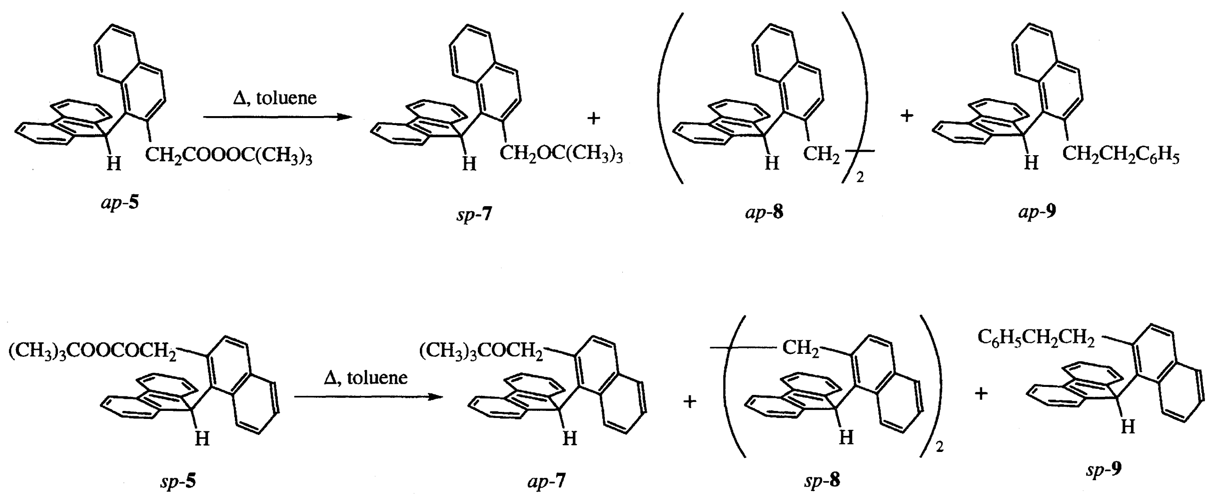


Scheme 2.



Scheme 3.

rates of decomposition and factors that influence the rates and little attention is paid to the products. Rates of decomposition of *t*-butyl phenylperacetate were first reported by Bartlett and Simons.[6] *t*-Butyl phenylperacetate decomposes to give ca. 20% benzyl *t*-butyl ether under ordinary conditions,[7] although under high pressures[8] or in viscous solvents[9] an enhanced cage effect causes formation of the compound in better yields. It seems that hydrogen abstraction by the benzyl radical is not a preferred process, because even in isopropylbenzene the formation of toluene occurs in



Scheme 4.

Table 1. Product Distributions of Thermolyses of *t*-Butyl [*ap*- and *sp*-1-(9-Fluorenyl)-2-naphthyl]peracetates in Toluene

Rotamer	**7**[b)]	**8**	**9**
ap	32	20	48
sp[a)]	18	38	44

a) The starting material was recovered in 9% yield. b) Stereochemical designation is reversed from the starting material.

very low yields. In agreement with these reports, we did not detect any 1-(9-fluorenyl)-2-methylnaphthalene[10] in the product.

Examination of Table 1 indicates that the formation of *ap*-**7** from *sp*-**5** is not much different from the distribution of *t*-butoxymethylbenzene from *t*-butyl phenylperacetate, whereas the formation of *sp*-**7** from *ap*-**5** is definitely a more preferred process than the case of *sp*-**5**. While the yields of bibenzyl in thermolyses of *t*-butyl phenylperacetate are in the range of 20%, a small amount of toluene (6%) is produced in cumene.[8] The yield of the dimer *ap*-**8** in the present case is comparable with these results for the *ap*, but that of the dimer *sp*-**8** is doubled with respect to *ap*-**8**. The cause for this phenomenon is not well understood, but is likely to be the results of different steric environments of the two radical centers. Comparison of the formation ratios of the products from the rotameric **5** indicates that *ap*-**5** gives less *ap*-**8**, whereas *sp*-**5** gives more *sp*-**8** than the counterpart. The radical center in *sp*-**1** is located at a more sterically crowded site than that in *ap*-**1**. Thus, *sp*-**1** has more chance to escape the cage before colligation to form *ap*-**7**, whereas the colligation in the cage is easier for *ap*-**1** than the counter part of the rotamers.

One feature of the product distributions in the thermolyses of **5** is that another colligation product, compound **9**, is abundantly obtained from both isomers. They are almost equally produced from the two isomers. These results imply that the radicals formed are much more stable than the benzyl radical. Since radicals **1** are hardly able to abstract hydrogen from toluene, the formation of **9** must be the colligation of **1** with the benzyl radical which is formed by abstraction of the α-hydrogen of toluene by the *t*-butoxyl radical. The almost equal formation of **9** from both rotamers is not well understood, although the high yields of the out-of-cage products, **8** and **9**, speaks for the sluggish reactivity of the radicals **1**, which is due to the steric effects: Even *ap*-**1** is sterically more protected than a benzyl radical because of the presence of a bulky substituent in the ortho position.

In summarizing the comparison of the product distributions in the thermolysis of **5** in toluene, we may conclude that the gross features are similar, although there are some significant differences. These differences are attributed to steric effects.

In Halogenated Methanes. There is little study in the literature on solvent effects on distribution of products from the decomposition of *t*-butyl phenylperacetate. Rüchardt and co-workers reported the results of thermolysis of the compound in carbon tetrachloride in the presence of bromotrichloromethane.[11] They found that the selectivity of the benzyl radicals, Br/Cl, is better than that of alkyl or aryl radicals owing to the stability of the benzyl radical; thus very little benzyl chloride, a chlorine-abstraction product, is produced. We have reported thermolyses of rotamers of peroxyesters in the triptycene series in carbon tetrachloride: The chlorine-abstraction products were obtained to some degree but no colligation product between the produced radical and the trichloromethyl was found.[4]

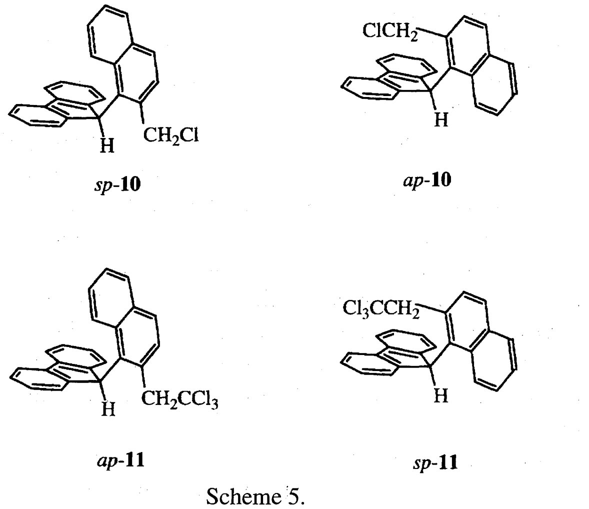
Although products from the decomposition of *t*-butyl phenylperacetate in carbon tetrachloride have not been carefully studied, those from dibenzoyl peroxide[12] and bis(1-naphthoyl) peroxide[13] in carbon tetrachloride are known. Products which contain at least one chlorine atom are aryl chlorides, in which a chlorine atom substitutes the perbenzoylcarbonyl group, and compounds with an aromatic ring substituted by a trichloromethyl group, the substitution of which occurred at the 4-position of the ring from the perbenzoylcarbonyl group, are also produced. The latter is attributed to the induced decomposition of the peroxide by a trichloromethyl radical which adds to the aromatic ring.

We did not observe the formation of a nucleus-substituted compound by a trichloromethyl radical, but a chlorine abstraction product (**10**) as well as a colligation product (**11**) between **1** and a trichloromethyl radical were detected (Scheme 5). The formation of the latter should be ascribed to the stability of the benzylic radical (**1**), which survives long enough to escape from the cage and to encounter the trichloromethyl radical.

Our data in Table 2, which compiles the product distributions from the thermolyses of **5** in carbon tetrachloride, show that a chloro compound (**10**) was the major product together with the *t*-butoxy compound (**7**). Interestingly, colligation products (**11**) from the solvent radical and the parent radical were produced in significant amounts. The better yield of *sp*-**11** for the *sp* form than that of *ap*-**11** from the *ap* again speaks for the low reactivity of radical *sp*-**1**. The yields of **8** significantly decreased with respect to the case of the thermolyses in toluene, but again the yield of *ap*-**8** is significantly higher than that of *sp*-**8**.

The structure of **11** was proved by independent syntheses. 2-Chloromethyl-1-(9-fluorenyl)naphthalene (**10**) was treated with lithium trichloromethanide,[14] which was prepared by treating carbon tetrachloride with butyllithium at −100 °C. The yields were not excellent but agreeable.

That we did not detect any colligation products such as **11** in the case of the triptycene series[4] should be ascribed to the instability of the primary alkyl radical which was generated from the mentioned compound. We may conclude that, if the radicals are stable, a considerable amount of trichloromethyl compounds should be produced from the thermal decomposition of peroxy compounds in carbon tetrachloride.



sp-**10** *ap*-**10**

ap-**11** *sp*-**11**

Scheme 5.

It is also true that *sp*-**5** is less readily decomposed than *ap*-**5** in carbon tetrachloride. Due to the low temperature of the thermolyses in carbon tetrachloride, even *ap*-**5** afforded 14% unreacted peroxy ester after 2 h at the boiling point of the solvent. *sp*-**5** showed that it reacted only to the extent of 50% under the conditions.

In chloroform, the conversion rates are still lower than those in carbon tetrachloride due to the fact that chloroform boils at a lower temperature than carbon tetrachloride: Due to the low conversion rates, the yields of the products may contain larger errors than other cases. Although the product distributions shown in Table 3 may thus contain large errors, yet it is apparent that no hydrogen-abstraction products were detected, while the cage product **7**, the dimer **8**, and the colligation products **11** were found in almost the same amounts. Such results imply that, although the benzylic radicals **1** are not able to abstract a hydrogen from chloroform, a *t*-butoxyl radical which is formed simultaneously can abstract a hydrogen from chloroform to produce the trichloromethyl radical, which reacts with the benzylic radical **1** to produce **11**.

In summary of the thermolyses of *t*-butyl peroxyesters, the peroxyesters behave very similarly irrespective of the rotameric positions, whereas the rates seem to be a little larger for the *ap* form than for the *sp* one. The reasons for the similarity must be that the peroxyester moieties as well as the radical centers in both rotamers contain no other functional groups than the peroxyester. We believe the main cause for the small differences is that the effectiveness of the steric effects that protect the radical intermediates **1** is different from one to another.

Photolyses of 2(1*H*)-Thioxo-1-pyridyl Esters. The esters were prepared in standard methods[15] and photolyzed at room temperature in an appropriate solvent without purification. The yields are often not reproducible, especially because purification of **6** was difficult due to its instability on being illuminated. Carboxylic acids **4** were often recovered from the products, suggesting that the conversion of **4** to **6** was not complete in many cases. The results shown in Table 4 are one of the best sets we obtained (Scheme 6). The yields of the products seem to be dependent on the purity of **6**, as will be described later.

In toluene, the dimer *ap*-**8** was produced abundantly with minor amount of the colligation product *sp*-**12** from *ap*-**6**. From *sp*-**6**, about the same yields of *ap*-**12** and *sp*-**8** with

Table 2. Product Distributions of Thermolyses of *t*-Butyl [*ap*- and *sp*-1-(9-Fluorenyl)-2-naphthyl]peracetates in Carbon Tetrachloride

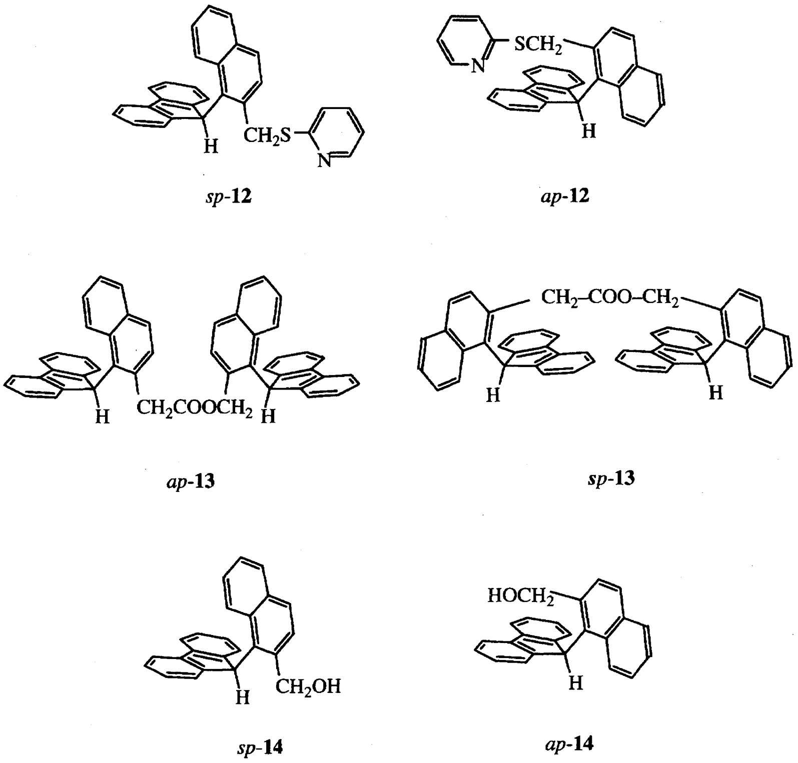
Rotamer	**7**[b)]	**8**	**10**[b)]	**11**
ap[a)]	41	7	40	11
sp[a)]	30	15	30	25

a) The starting material was recovered in 14% yield for *ap*, whereas that for *sp* 50%. b) Stereochemical designation is reversed from the starting material.

Table 3. Product Distributions of Thermolyses of *t*-Butyl [*ap*- and *sp*-1-(9-Fluorenyl)-2-naphthyl]peracetates in Chloroform

Rotamer	**7**[b)]	**8**	**11**
ap[a)]	24	35	41
sp[a)]	37	32	32

a) The starting material was recovered in 39% yield for *ap*, whereas that for *sp* 81%. b) Stereochemical designation is reversed from the starting material.



Scheme 6.

Table 4. Isolated Yields of Products in Photolyses of 2(1*H*)-Thioxo-1-pyridyl [1-(9-Fluorenyl)-2-naphthyl]acetate in Toluene and in Carbon Tetrachloride

Rotamer	Solvent	**8**	**10**[a)]	**12**[a)]	**4**
ap	Toluene	62	—	23	Trace
ap	CCl_4	23	3	51	Trace
sp	Toluene	59	—	25	Trace
sp	CCl_4	41	3	32	3

a) Stereochemical designation is reversed from the starting material.

those from *ap*-**6** were obtained. The carboxylic acid **4** was obtained only in trace amounts. The reasons are not well understood.

In carbon tetrachloride, the dimer **8** was more abundantly obtained from *sp*-**6** than from *ap*-**6**, whereas *sp*-**12** was the preferred product from *ap*-**6** with respect to *ap*-**12** from *sp*-**6**. This difference is again attributed to the steric environments of the radical centers: The less crowded *ap*-**1** can react in-cage to produce more *sp*-**12**, and the reverse is the case for *sp*-**1**. The expected chloro compounds (**10**) were produced only in 3% yields. It is difficult to discuss the distributions of **10**, because of their low yields.

The results compiled in Table 4 show that the products were obtained in ca. 80% yields in total. In some cases these high total yields were not realized for *sp*-**6**. Especially when the thioxopyridyl ester is crude, carboxylic acids **4** are recovered in large amounts. In order to get information about the product ratios in these cases, we separated minor products. It was shown that the ratios **8**/**12** decreased considerably (see Experimental), when a large amount of **4** is recovered. The causes for these phenomena may include the presence of the unreacted sodium salt of 2-mercaptopyridine 1-oxide or its free form, or else the unreacted carboxylic acids (**2**) and/or the corresponding acid chlorides have influenced the outcome. The details are not known.

Photolyses of *ap*-**6** in toluene afforded three minor products, when the conversion to *ap*-**6** was not complete. Although the assignments of the structures of two products were not possible because of the limited quantities, one of them crystallized. Its X-ray structure, though the *R* value never gets good enough for publication because of the presence of half a mole of dichloromethane as the solvent of crystallization which evaporates during the treatment, suggested that it must be an ester *ap*-**13**. We decided to synthesize this compound independently. Because the corresponding acid *ap*-**4** and the alcohol (*sp*-**14**) were available, the synthesis was easily accomplished to prove that this is really the compound. *ap*-**13** was obtained in 23% yield from the photolysis of *ap*-**6** in one case. The mechanism of formation of this ester *ap*-**13** must be the induced decomposition of *sp*-**6** by the radical *sp*-**1**.

By finding the formation of *ap*-**13** from *ap*-**6**, we were interested to know whether the isomeric ester *sp*-**13** is formed from *sp*-**6**. The ester *sp*-**13** was independently synthesized, but was never observed in the product mixtures from *sp*-**6**. We believe this is due to the steric protection of *sp*-**1**, which makes the induced decomposition difficult, but *ap*-**1** is less protected than *sp*-**1** to make it possible to induce decomposition of *sp*-**6**.

Experimental

The ^{1}H NMR spectra were recorded on a Varian Gemini-300 spectrometer which operated at 300.1 MHz and the infrared on a Hitachi I-2000 spectrometer. The elemental analyses were carried out on a Perkin–Elmer 240C analyzer. The HPLC machines were either Hitachi L-6250 or a Shimadzu LC-8A with UV detectors at 254 nm. Mass spectra (FAB) were recorded on a JEOL HX-110S spectrometer installed at Kyushu University. The yields of 1,2-bis-[1-(9-fluorenyl)-2-naphthyl]ethanes and the ester **13** are reported by doubling the actual moles, because they contain two fluorenylnaphthalene moieties. Melting points are not corrected. The product distribution was determined by ^{1}H NMR spectra before separation of the products.

Methyl [*ap*-1-(9-Fluorenyl)-2-naphthyl]acetate (*ap*-3). A solution of 4.76 g (14.2 mmol) of *sp*-(9-fluorenyl)naphthalene-2-carboxylic acid (*sp*-**2**)[16] and 12.0 mL of oxalyl dichloride (0.140 mol) in 70 ml of ether was stirred for 24 h at room temperature and the volatile materials were removed in vacuo. The resulting chloride was dissolved in 150 mL of ether and the solution was added to 600 mL of a diazomethane solution[17] in ether prepared from 20.6 g of potassium hydroxide in 100 mL of water and 10.1 g of *N*-nitrosomethylurea (98.3 mmol) in 700 mL of ether during a period of 45 min. The mixture was allowed to react for 2 h at room temperature. The excess diazomethane and the solvent were evaporated by introducing the gases into a dilute acetic acid and the residue was dissolved in 300 mL of methanol. To this solution was added 2.14 g (9.23 mmol) of freshly prepared silver oxide and the whole was heated under reflux for 1 h. The mixture was cooled and the solid removed by filtration. The solvent was removed from the filtrate and the residue was submitted to silica gel column chromatography with a 25 : 1 hexane-ethyl acetate eluent. The first fraction was the desired compound (3.94 g or 76% yield) and the second fraction was methyl *sp*-1-(9-fluorenyl)-2-naphthoate (246 mg or 5% yield). The latter compound was identical with an authentic specimen[18] in every respect. The title compound was purified by recrystallization from hexane-dichloromethane, mp 126.0—127.5 °C. Found: C, 85.94; H, 5.49%. Calcd for $C_{26}H_{20}O_2$: C, 85.68; H, 5.54%. ^{1}H NMR ($CDCl_3$) δ = 3.72 (3H, s), 4.21 (2H, s), 5.69 (1H, s), 6.45 (1H, d, J = 8.7 Hz), 6.82 (1H, ddd, J = 8.5, 6.8, and 1.4 Hz), 7.13—7.22 (5H, m), 7.38—7.44 (2H, m), 7.51 (1H, d, J = 8.5 Hz), 7.71 (1H, dd, J = 8.2 and 0.8 Hz), 7.79 (1H, d, J = 8.5 Hz), 7.94 (2H, t, J = 7.5 Hz).

Methyl [*sp*-1-(9-Fluorenyl)-2-naphthyl]acetate (*sp*-3). A solution of 6.67 g of the *ap*-isomer **3** in 200 ml of toluene was heated under reflux for 22 h and then the solvent was evaporated in vacuo. The residue (1 : 2.1 mixture of *sp* and *ap* isomers) was submitted to silica gel chromatography (7 : 1 hexane–dichloromethane), when a part of the *sp*-isomer and a part of *ap*-isomer were obtained. Finally, the separation of the mixture, which was not separated by usual column chromatography, was performed by HPLC over a silica gel column with a 1 : 1 hexane–dichloromethane eluent and a flow rate 40 ml min^{-1} (pressure 72 kg cm^{-2}). Under these conditions, the retention times of the *sp* and *ap* esters were 8.45 and 15.0 min, respectively. The yield of the *sp*-isomer was 30%, whereas 67% *ap*-isomer was recovered. The *sp*-ester *sp*-**3** was recrystallized from dichloromethane–hexane, mp 159.0—160.5 °C. Found: C, 85.84; H, 5.49%. Calcd for $C_{26}H_{20}O_2$: C, 85.68: H, 5.54%. ^{1}H NMR ($CDCl_3$) δ = 2.72 (2H, s), 3.02 (3H, s), 6.16 (1H, s), 7.12 (2H, dd, J = 7.6 and 0.8 Hz), 7.19—7.25 (3H, m), 7.39—7.44 (2H, m), 7.58 (1H, ddd, J = 8.1, 6.8, and 1.3 Hz), 7.64 (1H, ddd, J = 8.4, 6.8, and 1.6 Hz), 7.83 (1H, d, J = 8.5 Hz), 7.91 (2H, dd, J = 7.6 and 0.8 Hz), 7.96 (1H, dd, J = 8.0 and 1.6 Hz), 8.53 (1H, d, J = 8.6 Hz).

[1-(9-Fluorenyl)-2-naphthyl]acetic Acid (4). A solution of 2.96 g (8.12 mmol) of the foregoing methyl *ap*-ester in 150 mL of acetic acid was heated with 120 ml of concentrated hydrochloric acid for 4 h at 70 °C. The mixture was poured into water and the solid was collected by filtration. *ap*-[1-(9-Fluorenyl)-2-naphthyl]acetic acid (*ap*-**4**) was purified by recrystallization from dichloromethane–hexane, the yield being 96%. Mp 191.5—192.5 °C. Found: C, 85.69; H, 5.18%. Calcd for $C_{25}H_{18}O_2$: C, 85.43; H, 5.22%. ^{1}H NMR ($CDCl_3$) δ = 4.23 (2H, s), 5.63 (1H, s), 6.44 (1H, d, J = 8.7 Hz), 6.82 (1H, ddd, J = 8.6, 6.3, and 1.3 Hz), 7.10—7.11 (4H, m), 7.20 (1H, ddd, J = 8.0, 6.8, and 1.0 Hz), 7.33—7.38 (2H, m), 7.49 (1H, d, J = 8.4 Hz), 7.71 (1H, dd, J = 8.0 and 0.8 Hz).

sp-**4** was prepared similarly in 90% yield and recrystallized from the same solvent as above, mp 180.5—182.5 °C. Found: C, 85.34; H, 5.15%. Calcd for $C_{25}H_{18}O_2$: C, 85.43; H, 5.22%. ^{1}H NMR ($CDCl_3$) δ = 2.73 (2H, s), 6.16 (1H, s), 7.11 (2H, d, J = 6.9 Hz), 7.17 (2H, dt, J = 7.2 and 1.1 Hz), 7.19 (1H, d, J = 8.5 Hz), 7.39 (2H, t, J = 7.0 Hz), 7.58 (1H, ddd, J = 7.9, 6.8, and 1.1 Hz), 7.65 (2H, ddd, J = 8.6, 6.9, and 1.7 Hz), 7.84 (1H, d, J = 8.5 Hz), 7.88 (2H, d, J = 7.7 Hz), 7.96 (1H, dd, J = 7.9 and 1.4 Hz), 8.54 (1H, d, J = 8.6 Hz).

***t*-Butyl [*ap*-1-(9-Fluorenyl)-2-naphthyl]peracetate (*ap*-5).** *ap*-**4** (225 mg or 0.643 mmol) was converted to acid chloride with use of oxalyl dichloride as described for the preparation of **3**. To the crude acid chloride in 20 mL of dichloromethane was added a solution of anhydrous *t*-butyl hydroperoxide in dichloromethane[19] (1.0 ml or 11.6 mmol) and 0.21 mL of pyridine (2.57 mmol), and the whole was heated at 40 °C for 2 h. The mixture was washed with 1 mol dm^{-3} hydrochloric acid, with water, and finally with aqueous sodium hydrogencarbonate. The desired compound was purified by TLC on silica gel with a 1 : 2 hexane–dichloromethane eluent and recrystallized from 1 : 2 hexane–dichloromethane, mp 51.0—52.5 °C. The yield was 68%. Found: C, 82.62; H, 6.21%. Calcd for $C_{29}H_{26}O_3$: C, 82.44; H, 6.20%. ^{1}H NMR ($CDCl_3$) δ = 1.27 (9H, s), 4.22 (2H, s), 5.70 (1H, s), 6.47 (1H, d, J = 8.6 Hz), 6.83 (1H, ddd, J = 8.6, 6.9, and 1.4 Hz), 7.17—7.23 (5H, m), 7.38—7.44 (2H, m), 7.52 (1H, d, J = 8.5 Hz), 7.72 (1H, d, J = 8.3 Hz), 7.80 (1H, d, J = 8.5 Hz), 7.94 (2H, d, J = 7.6 Hz).

***t*-Butyl [*sp*-1-(9-Fluorenyl)-2-naphthyl]peracetate (*sp*-5).** Mp 87—105 °C (decomp), was similarly prepared in 81% yield and purified by recrystallization from 1 : 2 hexane-dichloromethane. Found: C, 82.60; H, 6.11%. Calcd for $C_{29}H_{26}O_3$: C, 82.44; H, 6.20%. ^{1}H NMR ($CDCl_3$) δ = 1.05 (9H, s), 2.72 (2H, s), 6.17 (1H, s), 7.15 (2H, dd, J = 7.5 and 0.8 Hz), 7.24 (2H, dt, J = 7.3 and 1.1 Hz), 7.27 (1H, d, J = 7.7 Hz), 7.42 (2H, t, J = 7.5 Hz), 7.60 (1H, ddd, J = 7.8, 6.8, and 1.0 Hz), 7.66 (1H, ddd, J = 8.6, 6.8, and 1.7 Hz), 7.83 (1H, d, J = 8.5 Hz), 7.90 (2H, d, J = 7.7 Hz), 7.97 (1H, dd, J = 8.4 and 1.6 Hz), 8.54 (1H, d, J = 8.5 Hz).

Thermolyses of *t*-Butyl [1-(9-Fluorenyl)-2-naphthyl]peracetate (5). The *t*-butyl ester (**5**) was weighed (ca. 200 mg) and dissolved in 20 mL of an appropriate solvent. The solution was degassed by immersing it in an ultrasonic bath for 10 min and heated at 80 °C for 4 h for toluene solutions or heated under reflux for carbon tetrachloride or chloroform solutions. The progress of the reactions was monitored by TLC. The solvent was removed in vacuo and the residue was submitted to preparative TLC on silica gel with a 2 : 1 hexane–dichloromethane eluent.

The *ap*-compound in toluene gave 3 bands in the TLC at R_f's 0.48, 0.37, and 0.29. The first fraction was *ap*-1-(9-fluorenyl)-2-(2-phenylethyl)naphthalene (*ap*-**9**), the second fraction was 1,2-bis-[*ap*-1-(9-fluorenyl)-2-naphthyl]ethane (*ap*-**8**), and the third was *sp*-

2-(*t*-butoxymethyl)-1-(9-fluorenyl)naphthalene (*sp*-**7**). They were obtained in 35, 24, and 27% yields, respectively. The formation ratios determined by ^{1}H NMR are given in Table 1. The identifications of these compounds are done by independent syntheses, which are described below, or by ^{1}H NMR and elemental analyses. No starting material was recovered.

***sp*-2-(*t*-Butoxymethyl)-1-(9-fluorenyl)naphthalene (*sp*-7):** This compound was synthesized independently as is described below and was identical with the compound obtained here.

1,2-Bis[*ap*-1-(9-fluorenyl)-2-naphthyl]ethane (*ap*-8): Recrystallized from dichloromethane–hexane, mp 248.0—248.5 °C. Found: C, 94.61; H, 5.67%. Calcd for $C_{48}H_{34}$: C, 94.39; 5.61%. MS (FAB, *o*-nitrophenyl octyl ether matrix): Found: *m*/*z* M$^+$, 610.3. Calcd for $C_{48}H_{34}$: M$^+$, 610.3. ^{1}H NMR ($CDCl_3$) δ = 3.74 (4H, s), 5.90 (2H, s), 6.40 (2H, dd, J = 8.7 and 0.8 Hz), 6.80 (2H, ddd, J = 8.5, 6.9, and 1.4 Hz), 7.01 (4H, dd, J = 7.6 and 0.8 Hz), 7.05 (4H, dt, J = 7.6 and 1.1 Hz), 7.16 (2H, ddd, J = 7.9, 6.8, and 1.0 Hz), 7.36—7.40 (4H, m), 7.46 (2H, d, J = 8.4 Hz), 7.65—7.67 (2H, m), 7.67 (2H, d, J = 8.5 Hz), 7.93 (4H, d, J = 7.7 Hz).

***ap*-1-(9-Fluorenyl)-2-(2-phenylethyl)naphthalene (*ap*-9):** Recrystallized from hexane, mp 119.5—120.0 °C. Found: C, 93.96; H, 6.19%. Calcd for $C_{31}H_{24}$: C, 93.90; H, 6.10%. ^{1}H NMR ($CDCl_3$) δ = 3.16—3.22 (2H, m), 3.43—3.48 (2H, m), 5.63 (1H, s), 6.41 (1H, d, J = 8.5 Hz), 6.81 (1H, ddd, J = 8.4, 6.8, and 1.3 Hz), 7.10—7.31 (10H, m), 7.42 (2H, t, J = 7.4 Hz), 7.45 (1H, d, J = 8.4 Hz), 7.69 (1H, d, J = 8.0 Hz), 7.74 (1H, d, J = 8.2 Hz), 7.97 (2H, d, J = 7.6 Hz).

The product from *sp*-**5** in toluene gave 4 bands at R_f's 0.56, 0.42, 0.31, and 0.07. The first fraction was *sp*-1-(9-fluorenyl)-2-(2-phenylethyl)naphthalene (*sp*-**9**), the second was 1,2-bis[*sp*-1-(9-fluorenyl)-2-naphthyl]ethane (*sp*-**8**), the third was *ap*-2-(*t*-butoxymethyl)-1-(9-fluorenyl)naphthalene (*ap*-**7**), and the fourth was recovered *t*-butyl peroxyester (*sp*-**5**). The yields were 36, 30, 13, and 9%, respectively.

***ap*-2-(*t*-Butoxymethyl)-1-(9-fluorenyl)naphthalene (*ap*-7):** This compound was synthesized independently as is described below and was found to be identical with the compound obtained here.

1,2-Bis[*sp*-1-(9-fluorenyl)-2-naphthyl]ethane (*sp*-8): Recrystallized from dichloromethane–hexane, mp 276.0—276.5 °C. Found: C, 94.54; H, 5.56%. Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61%. MS (FAB, *o*-nitrophenyl octyl ether matrix): Found : *m*/*z* M$^+$, 610.3. Calcd for $C_{48}H_{34}$: M$^+$, 610.3. ^{1}H NMR ($CDCl_3$) δ = 1.32 (4H, s), 5.58 (2H, d, J = 8.6 Hz), 6.01 (2H, s), 7.01 (4H, d, J = 7.6 Hz), 7.15 (4H, dt, J = 7.5 and 1.0 Hz), 7.41 (4H, t, J = 7.5 Hz), 7.45—7.55 (6H, m), 7.84 (2H, dd, J = 8.0 and 1.5 Hz), 7.97 (4H, d, J = 7.6 Hz), 8.37 (2H, d, J = 8.5 Hz).

***sp*-1-(9-Fluorenyl)-2-(2-phenylethyl)naphthalene (*sp*-9):** Recrystallized from dichloromethane–ether–hexane, mp 124.5—125.5 °C. Found: C, 94.08; H, 6.32%. Calcd for $C_{31}H_{24}$: C, 93.90; H, 6.10%. ^{1}H NMR ($CDCl_3$) δ = 1.91—1.97 (2H, m), 2.09—2.15 (2H, m), 6.19 (1H, s), 6.49 (1H, d, J = 7.4 Hz), 6.50 (1H, d, J = 7.9 Hz), 7.03—7.11 (3H, m), 7.18—7.24 (4H, m), 7.29 (1H, d, J = 8.5 Hz), 7.40—7.45 (2H, m), 7.56 (1H, ddd, J = 8.0, 6.9, and 1.1 Hz), 7.64 (1H, ddd, J = 8.4, 6.8, and 1.5 Hz), 7.82 (1H, d, J = 8.5 Hz), 7.92 (2H, d, J = 7.8 Hz), 7.95 (1H, dd, J = 8.0 and 1.6 Hz), 8.54 (1H, d, J = 8.8 Hz).

The product from *ap*-**5** in carbon tetrachloride gave 4 bands at R_f's 0.65, 0.55, 0.46, and 0.11 in the TLC. The first fraction was a mixture of *sp*-2-chloromethyl-1-(9-fluorenyl)naphthalene (*sp*-**10**) and *ap*-1-(9-fluorenyl)-2-(2,2,2-trichloroethyl)naphthalene (*ap*-**11**): These were separated by another TLC with a 9 : 1 hexane–dichloromethane eluent, when the trichloro compound was more easily eluted than the chloro. The second fraction was *ap*-**8**, the third *sp*-**7**, and the fourth the recovered starting material. The yields were 33, 6, 24, 12, and 14%, respectively, for *sp*-**7**, *ap*-**8**, *sp*-**10**, *ap*-**11**, and the starting material. Their distribution before isolation is shown in Table 2. *ap*-**8** and *sp*-**7** were identical with those described in the thermolysis of *ap*-**5** in toluene. *sp*-**10** and *ap*-**11** were identical with the compounds independently synthesized below in every respect.

The product from *sp*-**5** in carbon tetrachloride gave 4 bands at R_f's 0.62, 0.41, 0.25, and 0.06 in the TLC. The first fraction was a mixture of *ap*-**10** and *sp*-**11**, which was further separated by TLC with 8 : 1 hexane–dichloromethane, when *sp*-**11** was more easily eluted than *ap*-**10**. The second fraction was *sp*-**8**, the third *ap*-**7**, and the fourth the starting material. The yields were 13, 6, 11, 10, and 50%, respectively, for *ap*-**7**, *sp*-**8**, *ap*-**10**, *sp*-**11**, and *sp*-**5**. *sp*-**8** and *ap*-**7** were identical with those described in the thermolysis of the *sp*-compound in toluene. *ap*-**10** and *sp*-**11** were identical with the compounds independently synthesized below in every respect.

The product from *ap*-**5** in chloroform gave 4 bands in TLC at R_f's 0.61, 0.45, 0.34, and 0.11. The first fraction was *sp*-**11**, the second the *ap*-**8**, the third *ap*-**7**, and the fourth the starting material. The yields were 10, 18, 19, and 39%, respectively. No *sp*-**10** was detected. The identification of these compounds is described elsewhere in this paper.

The product from *sp*-**5** in chloroform gave 4 bands in the TLC at R_f's 0.63, 0.47, 0.27, and 0.10. The first fraction was *ap*-**11**, the second *sp*-**8**, the third *sp*-**7**, and the fourth starting material. The yields were 7, 6, 6, and 81%, respectively, for *ap*-**7**, *sp*-**8**, *sp*-**11**, and *sp*-**5**. No *ap*-**10** was detected. The identification of these compounds is described elsewhere in this paper.

***sp*-9-(2-Hydroxymethyl-1-naphthyl)fluorene (*sp*-14).** While this compound had been prepared by hydrolysis of the bromide,[20] it could be prepared by $LiAlH_4$ reduction of the corresponding methyl ester of *sp*-**2** in ether. ^{1}H NMR ($CDCl_3$) δ = 1.91 (1H, t, J = 5.5 Hz), 5.23 (2H, d, J = 5.5 Hz), 6.47 (1H, s), 6.48 (1H, d, J = 8.6 Hz), 6.83 (1H, dt, J = 7.9 and 1.4 Hz), 7.13—7.24 (5H, m), 7.41 (2H, t, J = 7.4 Hz), 7.64 (1H, d, J = 8.6 Hz), 7.72 (1H, d, J = 8.2 Hz), 7.82 (1H, d, J = 8.6 Hz), 7.95 (2H, d, J = 7.9 Hz).

***ap*-9-(2-Hydroxymethyl-1-naphthyl)fluorene (*ap*-14).** Thermal equilibration of the *sp* and the *ap*-isomers was accomplished by heating a toluene solution of *sp*-**14** under reflux for 18 h. The *ap*/*sp* ratio was 1 : 1.7. The mixture could be separated by chromatography on silica gel with a 7 : 1 hexane–ethyl acetate eluent, when the *ap* isomer was eluted first. This compound was identical with the authentic specimen.[20] ^{1}H NMR ($CDCl_3$) δ = 0.81 (1H, t, J = 6.8 Hz), 3.63 (2H, d, J = 6.8 Hz), 6.18 (1H, s), 7.18 (2H, d, J = 7.5 Hz), 7.24 (2H, dt, J = 1.0 and 7.3 Hz), 7.44 (2H, t, J = 7.4 Hz), 7.55 (1H, d, J = 8.5 Hz), 7.59 (1H, app t, J = 6.9 Hz), 7.66 (1H, ddd, J = 8.3, 6.8, and 1.6 Hz), 7.88 (1H, d, J = 8.5 Hz), 7.92 (2H, d, J = 7.7 Hz), 7.97 (1H, dd, J = 8.0 and 1.2 Hz), 8.56 (1H, d, J = 8.6 Hz).

Acetate of *sp*-14. Mp 111—112 °C, was prepared by treating the *sp*-alcohol with acetyl chloride and pyridine in dichloromethane. The product was purified by recrystallization from hexane-dichloromethane. Found: C, 85.50; H, 5.55%. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53%. ^{1}H NMR ($CDCl_3$) δ = 2.10 (3H, s), 5.26 (2H, s), 5.70 (1H, s), 6.49 (1H, d, J = 8.6 Hz), 6.84 (1H, t, J = 7.4 Hz), 7.13—7.27 (5H, m), 7.42 (2H, t, J = 7.4 Hz), 7.62 (1H, d, J = 8.6 Hz), 7.73 (1H, d, J = 8.2 Hz), 7.82 (1H, d, J = 8.6 Hz), 7.95 (2H, d, J = 7.5 Hz).

Isomerization of the *sp*-acetate was carried out by heating a solution of 150 mg of it in 10 mL of xylene for 18 h. The product consisted of 2.3 : 1 of *sp* and *ap* esters. The mixture was submitted to TLC with a 1 : 3 dichloromethane–hexane eluent. They were eluted in the order of *sp* and then *ap*.

Acetate of *ap*-14. Mp 93—94 °C, was purified by recrystallization from hexane–dichloromethane. Found: C, 85.54; H, 5.49%. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53%. ^{1}H NMR (CDCl$_3$) $\delta = 1.65$ (3H, s), 4.21 (2H, s), 6.21 (1H, s), 7.17 (2H, d, $J = 7.5$ Hz), 7.23 (2H, dt, $J = 7.4$ and 1.0 Hz), 7.35 (1H, d, $J = 8.6$ Hz), 7.42 (2H, t, $J = 7.5$ Hz), 7.62 (1H, dt, $J = 7.5$ and 1.4 Hz), 7.68 (1H, ddd, $J = 8.7$, 8.0, and 1.4 Hz), 7.86 (1H, d, $J = 8.6$ Hz), 7.90 (2H, d, $J = 7.9$ Hz), 7.98 (1H, dd, $J = 7.9$ and 1.4 Hz), 8.59 (1H, d, $J = 8.6$ Hz).

***sp*-9-(2-Chloromethyl-1-naphthyl)fluorene (*sp*-10).** To a solution of 1.0 g (3.1 mmol) of the preceding alcohol in 20 mL of dichloromethane was added a solution of 450 μL of thionyl chloride in 5.0 mL of dichloromethane; the mixture was heated under reflux for 2 h. The solvent and unreacted thionyl chloride were evaporated and the residue was submitted to column chromatography on silica gel (1 : 2 dichloromethane–hexane eluent). The chloride recrystallized from hexane–dichloromethane, mp 136.0—136.5 °C, was obtained in 66% yield. Found: C, 84.68; H, 5.17%. Calcd for $C_{24}H_{17}Cl$: C, 84.57; H, 5.07%. ^{1}H NMR (CDCl$_3$) $\delta = 5.11$ (2H, s), 5.85 (1H, s), 6.50 (1H, dd, $J = 8.9$ and 0.7 Hz), 6.85 (1H, ddd, $J = 8.6$, 6.9, and 1.4 Hz), 7.10—7.26 (5H, m), 7.38—7.47 (2H, m), 7.59 (1H, d, $J = 8.6$ Hz), 7.72 (1H, d, $J = 7.9$ Hz), 7.81 (1H, d, $J = 8.2$ Hz), 7.96 (2H, dd, $J = 7.5$ and 1.0 Hz).

***ap*-9-(2-Chloromethyl-1-naphthyl)fluorene (*ap*-10)** was obtained as a mixture with the *sp* isomer by heating a solution of the *sp* form in xylene for 20 h. The *ap*/*sp* ratio was 1/2.3. The mixture was separated by silica gel chromatography with 1 : 4 dichloromethane–hexane eluent. The *ap* isomer was eluted first and the *sp* isomer followed closely. The *ap* isomer was recrystallized from hexane–dichloromethane, mp 122.5—123.5 °C. Found: C, 84.64; H, 5.11%. Calcd for $C_{24}H_{17}Cl$: C, 84.57; H, 5.07%. ^{1}H NMR (CDCl$_3$) $\delta = 3.65$ (2H, s), 6.18 (1H, s), 7.18 (1H, dd, $J = 6.5$ and 0.7 Hz), 7.22—7.27 (3H, m), 7.41—7.49 (3H, m), 7.62—7.68 (2H, m), 7.87 (1H, d, $J = 8.6$ Hz), 7.91 (2H, dd, $J = 7.6$ and 1.0 Hz), 7.97 (1H, dd, $J = 7.9$ and 1.7 Hz), 8.56 (1H, d, $J = 8.4$ Hz).

***sp*-(2-*t*-Butoxymethyl)-1-(9-fluorenyl)naphthalene (*sp*-7).** A solution of 250 mg (0.78 mmol) of the alcohol *sp*-**14** in 10 mL of dichloromethane was mixed with ca. 2 mL of isobutene with ice-cooling. Two drops of sulfuric acid was added to the mixture and the whole was stirred for 2 h at 0 °C and then overnight at room temperature. The mixture was washed with aqueous sodium hydrogencarbonate and the solvent was evaporated. The residue was submitted to silica gel chromatography (1 : 2 dichloromethane–hexane eluent) to afford the desired compound in 54% yield. It was recrystallized from hexane–dichloromethane, mp 132—133 °C. Found: C, 88.92; H, 7.02%. Calcd for $C_{28}H_{26}O$: C, 88.85; H, 6.92%. ^{1}H NMR (CDCl$_3$) $\delta = 1.30$ (9H, s), 4.92 (2H, s), 5.82 (1H, s), 6.46 (1H, d, $J = 8.7$ Hz), 6.80 (1H, ddd, $J = 8.4$, 6.8 and 1.4 Hz), 7.15—7.26 (5H, m), 7.40 (2H, t, $J = 7.4$ Hz), 7.63 (1H, d, $J = 8.4$ Hz), 7.70 (1H, d, $J = 8.1$ Hz), 7.79 (1H, d, $J = 8.6$ Hz), 7.95 (2H, d, $J = 7.9$ Hz).

Isomerization of the *t*-butoxy compound **7** was carried out by heating a xylene solution of the *sp* compound for 17 h. The ratio *sp*/*ap* was 1.4/1 at the equilibrium. The mixture was chromatographed on silica gel with 1 : 30 ether–hexane: the *sp* compound was eluted first and then the *ap*. *ap*-**7** was recrystallized from hexane–dichloromethane, mp 105.5—106.5 °C. Found: C, 88.89; H, 7.05%. Calcd for $C_{28}H_{26}O$: C, 88.85; H, 6.92%. ^{1}H NMR (CDCl$_3$) $\delta = 0.70$ (9H, s), 3.31 (2H, s), 6.18 (1H, s), 7.17 (2H, d, $J = 7.5$ Hz), 7.22 (2H, dt, $J = 1.0$ and 7.5 Hz), 7.41 (2H, t, $J = 7.5$ Hz), 7.55 (1H, t, $J = 7.5$ Hz), 7.63 (1H, dt, $J = 1.7$ and 7.7 Hz), 7.65 (1H, d, $J = 8.6$ Hz), 7.84 (1H, d, $J = 8.6$ Hz), 7.90 (2H, d, $J = 7.5$ Hz), 7.95 (1H, d, $J = 7.9$ Hz), 8.54 (1H, d, $J = 8.6$ Hz).

***ap*-1-(9-Fluorenyl)-2-(2,2,2-trichloroethyl)naphthalene (*ap*-11).** To a solution of 424 mL (4.40 mmol) of carbon tetrachloride in 4 mL of tetrahydrofuran, was added 2.80 mL (4.40 mmol) of a 15% solution of butyllithium in hexane at −100 °C in 30 min; then the mixture was stirred at that temperature for 1 h. A solution of 544 mg (1.63 mmol) of *sp*-**10** in 2 mL of THF was added to the solution of trichloromethyllithium prepared above in 30 min; then the mixture was stirred for 7 h at the temperature. The mixture was quenched with water and extracted with ether. The ether extract was dried over magnesium sulfate and filtered. The solvent was evaporated and the residue was chromatographed on silica gel (1 : 5 dichloromethane–hexane eluent). The desired product was obtained in 40% yield. Unreacted chloromethyl compound was recovered to some extent. The analytical sample was purified by recrystallization from hexane–dichloromethane, mp 179—180 °C. Found: C, 70.68; H, 3.94%. Calcd for $C_{25}H_{17}Cl_3$: C, 70.86; H, 4.04%. ^{1}H NMR (CDCl$_3$) $\delta = 4.61$ (2H, s), 6.02 (1H, s), 6.50 (1H, d, $J = 8.9$ Hz), 6.85 (1H, ddd, $J = 8.8$, 7.0, and 1.4 Hz), 7.13 (2H, app d, $J = 6.8$ Hz), 7.19 (2H, dt, $J = 1.0$ and 7.4 Hz), 7.25 (1H, dt, $J = 1.0$ and 7.4 Hz), 7.43 (2H, t, $J = 7.5$ Hz), 7.75 (1H, d, $J = 7.5$ Hz), 7.83 (2H, s), 7.97 (2H, d, $J = 7.5$ Hz).

sp-Isomer (*sp*-**11**) was obtained by isomerization of the *ap*-isomer, by heating a xylene solution for 10 h, as a mixture of the rotamers. The *sp*/*ap* ratio was 1/4.2. They were separated by silica gel chromatography (hexane eluent): The *sp* isomer was eluted faster than the *ap*. The pure sample was obtained by recrystallization from hexane–dichloromethane, mp 145.5—146.0 °C. Found: C, 71.06; H, 3.89%. Calcd for $C_{25}H_{17}Cl_3$: C, 70.86; H, 4.04%. ^{1}H NMR (CDCl$_3$) $\delta = 3.16$ (2H, s), 6.23 (1H, s), 7.17—7.28 (4H, m), 7.44 (2H, t, $J = 7.4$ Hz), 7.63 (1H, t, $J = 7.4$ Hz), 7.69 (1H, dt, $J = 1.4$ and 7.7 Hz), 7.85—7.96 (4H, m), 7.99 (1H, d, $J = 8.2$ Hz), 8.61 (1H, d, $J = 8.2$ Hz).

2(1*H*)-Thioxo-1-pyridyl [1-(9-Fluorenyl)-2-naphthyl]acetate (6). A solution of ca. 200 mg (ca. 0.58 mmol) of the acid (**4**) and 1.0 ml (11.6 mmol) of oxalyl dichloride in 20 mL of benzene was stirred at room temperature for 2 h and then the volatile materials were removed in vacuo. The residue was taken up in 20 mL of an appropriate solvent and, to the solution, was added 114 mg (0.724 mmol) of the sodium salt of 2-mercaptopyridine 1-oxide. The residue, which was obtained in the preparation described above, was taken up in 20 ml of an appropriate solvent. To the solution were added 114 mg (ca. 0.724 mmol) of sodium salt of 1-mercaptopyridine 1-oxide and 11 mg (0.09 mmol) of 4-(dimethylamino)pyridine. The mixture was allowed to react overnight with protection from light by wrapping the flask with aluminium foil. After evaporating the solvent, the following ^{1}H NMR data (CDCl$_3$, δ) were recorded.

***ap*-6:** $\delta = 4.65$ (2H, s), 5.70 (1H, s), 6.48 (1H, d, $J = 9.2$ Hz), 6.58 (1H, dt, $J = 1.8$ and 6.9 Hz), 6.85 (1H, ddd, $J = 8.5$, 7.2, and 1.7 Hz), 7.15—7.26 (6H, m), 7.39—7.50 (3H, m), 7.63 (1H, d, $J = 8.5$ Hz), 7.68 (1H, dd, $J = 1.7$ and 8.8 Hz), 7.74 (1H, d, $J = 7.6$ Hz), 7.85 (1H, d, $J = 8.5$ Hz), 7.96 (2H, d, $J = 7.5$ Hz)

***sp*-6:** $\delta = 3.23$ (2H, s), 6.20 (1H, s), 6.51 (1H, dt, $J = 1.8$ and 6.8 Hz), 6.94 (1H, dd, $J = 1.5$ and 7.0 Hz), 7.11 (1H, ddd, $J = 1.5$, 7.2, and 8.5 Hz), 7.18 (2H, d, $J = 7.6$ Hz), 7.24—7.30 (2H, m), 7.41 (1H, d, $J = 8.5$ Hz), 7.48 (2H, t, $J = 7.6$ Hz), 7.56 (1H, dd, $J = 1.7$ and 8.9 Hz), 7.59—7.70 (2H, m), 7.88 (1H, d, $J = 8.3$ Hz), 7.94—8.01 (3H, m), 8.54 (1H, d, $J = 8.4$ Hz).

Photolyses of 6. The solution of the thioxopyridyl ester **6** in an appropriate solvent was degassed by immersing in a ultrasonic bath for 5 min under a nitrogen atmosphere. Then the solution was irradiated with an 18 W fluorescent lamp with stirring for 12 h at room temperature. During this period the color changed from yellow to orange. The orange color was persistent until the mixture was quenched, when the reaction was carried out in toluene. In the case of the reaction in carbon tetrachloride, the color further changed to colorless at the end of the reaction. The products were separated by preparative TLC with a 1 : 2 hexane–dichloromethane eluent.

In one run, the reaction mixture from *ap*-**6** in toluene afforded 5 fractions, R_f's being 0.86, 0.64. 0.43, 0.15, and 0.08 in the TLC. The second fraction was a mixture of two unknown compounds; they could be separated by HPLC (1 : 1 dichloromethane–hexane, 25 ml min^{-1} flow, 32 kg cm^{-2} pressure). The more easily eluted fraction (12.5 min retention time) and the less easily eluted fraction (retention time 14.8 min) were named **15** and **16**. The first fraction was *ap*-**8**, the third *sp*-**12**, the fourth an unknown compound (**17**), and the last the carboxylic acid (*ap*-**4**). The yields were 67.0 mg, 8.9 mg, 37.0 mg, 12.7 mg, 17.2 mg, and 35.9 mg, respectively, for *ap*-**4**, *ap*-**8**, *sp*-**12**, **17**, **15**, and **16**. Compound **16** was found to be identical with *ap*-**13** that was independently synthesized as described below. For the unknown compounds, the following spectroscopic data were recorded.

15: ^{1}H NMR (CDCl$_3$) δ = 6.75 (1H, s), 10.91 (1H, s), 14 aromatic protons. IR (Nujol®) 1694, 1620, 1598 cm^{-1}.

17: ^{1}H NMR (CDCl$_3$) δ = 5.23 (2H, s), 5.89 (1H, s), 14 aromatic protons. IR (Nujol®) 1736, 1464 cm^{-1}.

ap-**4** and *ap*-**8** were identical with the authentic specimens.

***sp*-1-(9-Fluorenyl)-2-(2-pyridylthiomethyl)naphthalene (*sp*-12)** was purified by recrystallization from dichloromethane–hexane, mp 182—183 °C. Found: C, 83.99; H, 5.15; N, 3.49%. Calcd for $C_{29}H_{21}NS$: C, 83.82; H, 5.09; N, 3.37%. ^{1}H NMR (CDCl$_3$) δ = 4.96 (2H, s), 5.95 (1H, s), 6.45 (1H, dd, J = 8.7 and 0.8 Hz), 6.82 (1H, ddd, J = 8.5, 4.8, and 1.4 Hz), 6.98 (1H, ddd, J = 7.3, 5.0, and 1.1 Hz), 7.16—7.25 (6H, m), 7.38—7.49 (3H, m), 7.68 (1H, d, J = 8.2 Hz), 7.72 (1H, d, J = 8.7 Hz), 7.77 (1H, d, J = 8.5 Hz), 7.94 (2H, d, J = 7.6 Hz), 8.42 (1H, ddd, J = 5.0, 1.9, and 0.9 Hz).

In one run, the reaction products from *sp*-**6** in toluene afforded 4 fractions in TLC (1 : 1 hexane–dichloromethane eluent), R_f's being 0.44, 0.32, 0.16, and 0.08. The first fraction (**18**) is an unknown compound, the second *ap*-**12**, the third another unknown (**19**), and the fourth *sp*-**4**. The yields of *sp*-**4**, *sp*-**8**, *ap*-**12**, **19**, and **18**, were 72.6 mg, 50.4 mg, 49.4 mg, 12.7 mg, and 11.0 mg, respectively. The following spectroscopic data were recorded for the unknown compounds.

18: ^{1}H NMR (CDCl$_3$) δ = 6.25 (1H, s), 6.75 (1H, s), 8.97 (1H, s), 10.91 (1H, s), 31—32 aromatic protons. IR (Nujol®) 1676, 1620, 1464 cm^{-1}.

19: ^{1}H NMR (CDCl$_3$): δ = 3.63 (2H, br s), 6.18 (1H, s), 8.56 (1H, d), 13 aromatic protons. IR (Nujol®) 3572, 3420, 1448 cm^{-1}.

The *ap*-acid **4** and the dimer **8** were identical with the authentic specimens.

***ap*-1-(9-Fluorenyl)-2-(2-pyridylthiomethyl)naphthalene (*ap*-12)** was purified by recrystallization from dichloromethane–hexane, mp 143—144 °C. Found: C, 84.14; H, 5.34; N, 3.07%. Calcd $C_{29}H_{21}NS$: C, 83.82; H, 5.09; N, 3.37%. ^{1}H NMR (CDCl$_3$) δ = 3.54 (2H, s), 6.21 (1H, s), 6.63 (1H, dd, J = 8.2 and 1.1 Hz), 6.85 (1H, ddd, J = 7.4, 4.9, and 1.1 Hz), 7.20—7.29 (5H, m), 7.40 (2H, dt, J = 7.0 and 0.7 Hz), 7.53 (1H, d, J = 8.5 Hz), 7.54—7.59 (1H, m), 7.65 (1H, ddd, J = 8.6, 6.8, and 1.6 Hz), 7.76 (1H, d, J = 8.5 Hz), 7.86 (2H, d, J = 7.9 Hz), 7.92 (1H, dd, J = 8.1 and 1.1 Hz), 8.25 (1H, ddd, J = 5.0, 1.9, and 1.0 Hz), 8.55 (1H, d, J = 8.7 Hz).

In one of the reactions of *ap*-**6** in carbon tetrachloride, the product mixture was separated by preparative TLC on silica gel with a 1 : 2 hexane–dichloromethane eluent, giving 4 bands. The R_f values were 0.51, 0.42, 0.13, and 0.03. The first fraction was *sp*-**10**, the second *ap*-**8**, the third *sp*-**12**, and the fourth *ap*-**4**. The yields were, 9.1 mg, 11.3 mg, 94.7 mg, and 61.0 mg, respectively. These compounds were identical with the authentic specimens. No trichloromethyl compound *sp*-**11** was detected in the mixture. Minor products observed in the same reaction of *ap*-**6** in toluene were not detected.

In one run, when the reaction product from *sp*-**6** in carbon tetrachloride was triturated with dichloromethane, the dimer *sp*-**8** (40.9 mg) remained undissolved and was collected by filtration. The remainder was separated into 4 fractions by preparative TLC with a 1 : 1 hexane–dichloromethane eluent. The R_f values were 0.53, 0.35, 0.17, and 0.06. The first fraction and the third were the same compounds with **15** and **16**, respectively. The second fraction and the fourth were *ap*-**12** and *sp*-**4**, respectively. The yields of **15**, *ap*-**12**, **16**, and *sp*-**4** were 8.6 mg, 72.5 mg, 13.1 mg, and 57.7 mg, respectively.

***sp*-[1-(9-Fluorenyl)-2-naphthyl]methyl *ap*-[1-(9-Fluorenyl)-2-naphthyl]acetate (*ap*-13).** To a solution of 100 mg (286 μmol) of the *ap*-acid *ap*-**4** and 92.0 mg (286 μmol) of *sp*-**14** in 5 mL of dichloromethane, was added 70.7 mg (343 μmol) of dicyclohexylcarbodiimide and 6.97 mg (57.2 μmol) of 4-(dimethylamino)pyridine, and the whole was stirred at room temperature for 24 h. The insoluble material was removed by filtration and the solvent was evaporated. The residue was recrystallized from hexane–dichloromethane, mp 220.5—221.5 °C. These crystals contained half a mole of dichloromethane as a solvent of crystallization. The yield was 32%. Found: C, 85.47; H, 5.17%. Calcd for $C_{49}H_{34}O_2\cdot 1/2(CH_2Cl_2)$: C, 85.27; H, 5.06%. ^{1}H NMR (CDCl$_3$): δ = 4.24 (2H, s), 5.42 (1H, s), 5.49 (1H, s), 5.67 (2H, s), 6.34 (1H, d, J = 9.3 Hz), 6.39 (1H, d, J = 8.7 Hz), 6.74—6.82 (2H, m), 6.92—6.99 (8H, m), 7.14—7.30 (6H, m), 7.45 (1H, d, J = 8.4 Hz), 7.54 (1H, d, J = 8.7 Hz), 7.66—7.82 (8H, m). IR (Nujol®) 1732 cm^{-1}.

***ap*-[1-(9-Fluorenyl)-2-naphthyl]methyl *sp*-[1-(-Fluorenyl)-2-naphthyl]acetate (*sp*-13).** This compound was prepared similarly from *sp*-**4** and *ap*-**14** in 44% yield. It was recrystallized from dichloromethane and then hexane–benzene, mp 207—208 °C. Found: C, 89.51; H, 5.27%. Calcd for $C_{49}H_{34}O_2$: C, 89.88; H, 5.23%. ^{1}H NMR (CDCl$_3$) δ = 2.41 (2H, s), 3.60 (2H, s), 6.02 (1H, s), 6.12 (1H, s), 6.92—6.94 (4H, m), 7.00—7.09 (4H, m), 7.14—7.21 (4H, m), 7.40 (2H, t, J = 7.5 Hz), 7.55—7.65 (4H, m), 7.75—7.79 (4H, m), 7.88—7.93 (4H, m), 8.45 (1H, d, J = 8.4 Hz), 8.53 (1H, d, J = 8.4 Hz). IR (Nujol®)1736 cm^{-1}.

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