Reactivities of Stable Rotamers XXXVII: Thermolyses and Photolyses of 2(1*H*)-Thioxo-1-pyridyl 3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoate Rotamers[1,2)]

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By decomposition of the title compounds, 2-(1,4-dimethyl-9-triptycyl)-2-methylpropyl radical rotamers were generated. In thermolysis the *ap*-isomer gave, as a main product, a cyclic compound which was formed by attack of the radical on the benzene ring in proximity, whereas extensive rearrangement took place to produce 1-substituted methyl derivatives in the case of *sc*. In photolysis, various out-of-cage products were found from both rotamers including dimers of radicals. The results are attributed to formation of high concentration of the radicals in photolyses. The product distributions are also affected by the phase, i. e. solution, melts, or solid, as well as temperature. Solid state photolyses afforded 2-pyridyl thioethers as almost exclusive products, suggesting that recombination of radicals in the cage is important under the conditions where movement of the radicals is restricted.

The reactivities of carbocations and carbon radicals generated at the rotameric positions have been studied by the use of the 9-alkyl substituted triptycene system.[1—5)] As an example of the radical reaction, we recently reported the Hunsdiecker chlorodecarboxylation of 3-(1,4-dimethyl-9-triptycyl)-3-methylbutanoic acid rotamers (*ap*-**3** and *sc*-**3**) in the presence of a chloride source and lead(IV) acetate:[4)] The reaction is known to proceed via a radical intermediate.[6)] The results reveal that the interaction of the radical center with the 1-methyl substituent is important in the *sc*-radical (*sc*-**1**), whereas such an interaction is negligible in the *ap*-radical (*ap*-**1**) because the radical center is far from the substituent (Chart 1).

Although the results of the chlorodecarboxylation provide valuable information on the fate of the rotameric radicals, there remain some ambiguities in discussing the reaction mechanism.[4)] Firstly, more than 60% of the starting carboxylic acid was recovered in the lead(IV) mediated reaction even though a large excess of the reagents was used. Although we discussed the reactivities with the exclusion of the recovered carboxylic acid, the origin, whether it is the product from the intermediate radical or unreacted species, was ambiguous. Also, the presence of the excess salts might affect the reaction mechanism. Secondly, the chlorodecarboxylation was frequently influenced by the quality of the lead reagent as well as the presence of oxygen in solvents as mentioned in the literature.[6)] Finally, the formation of a product from the *sc*-carboxylic acid, its acetonyl ester, was an unexpected result. The reaction mechanism for the formation of the compound is still unknown. In order to shed light on these problems and to confirm whether or not the reactivity we had observed for the chlorodecarboxylation was that of genuine carbon radicals, we wished to use another method for the generation of carbon radicals.

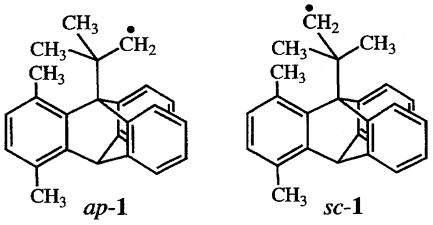
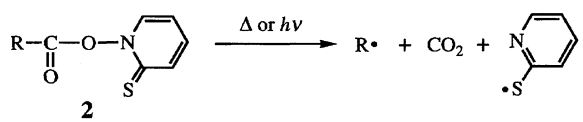


Chart 1.

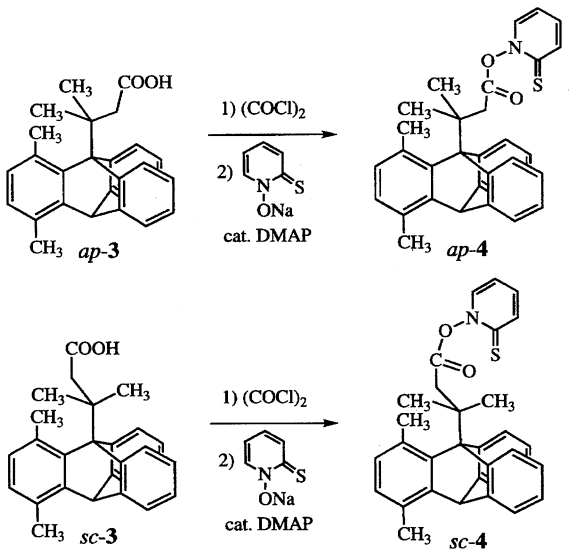
One of the convenient methods for the generation of alkyl radicals is decomposition of 2(1*H*)-thioxo-1-pyridyl esters (**2**), which was developed by Barton et al. and is now widely used for the organic transformations via radicals.[7—9)] The esters readily give alkyl radicals on heating or light irradiation in the absence of metal salts according to Scheme 1. We felt that this method was most suitable for the radical reactions of the triptycene compounds because the precursor was easily obtained from the carboxylic acid and the radicals could be generated under clean conditions. Therefore, the 2(1*H*)-thioxo-1-pyridyl esters of the rotameric carboxylic acids, *ap*-**4** and *sc*-**4**, were synthesized and the radical reactions were performed under various conditions. This paper describes the reactivities of the rotameric radicals and the factors affecting the reactions: rotational isomerism, solvent, method of radical generation, and mobility of molecular species.



Scheme 1.

Results

Synthesis and Spectroscopic Properties. Rotational isomers of 2(1*H*)-thioxo-1-pyridyl esters (*ap*-**4** and *sc*-**4**) were synthesized by the treatment of the corresponding acid chloride,[10] prepared from the carboxylic acids (**3**) and oxalyl dichloride, with sodium salt of *N*-hydroxypyridine-2(1*H*)-thione in the presence of a catalytic amount of 4-dimethylaminopyridine (Scheme 2).[11,12]



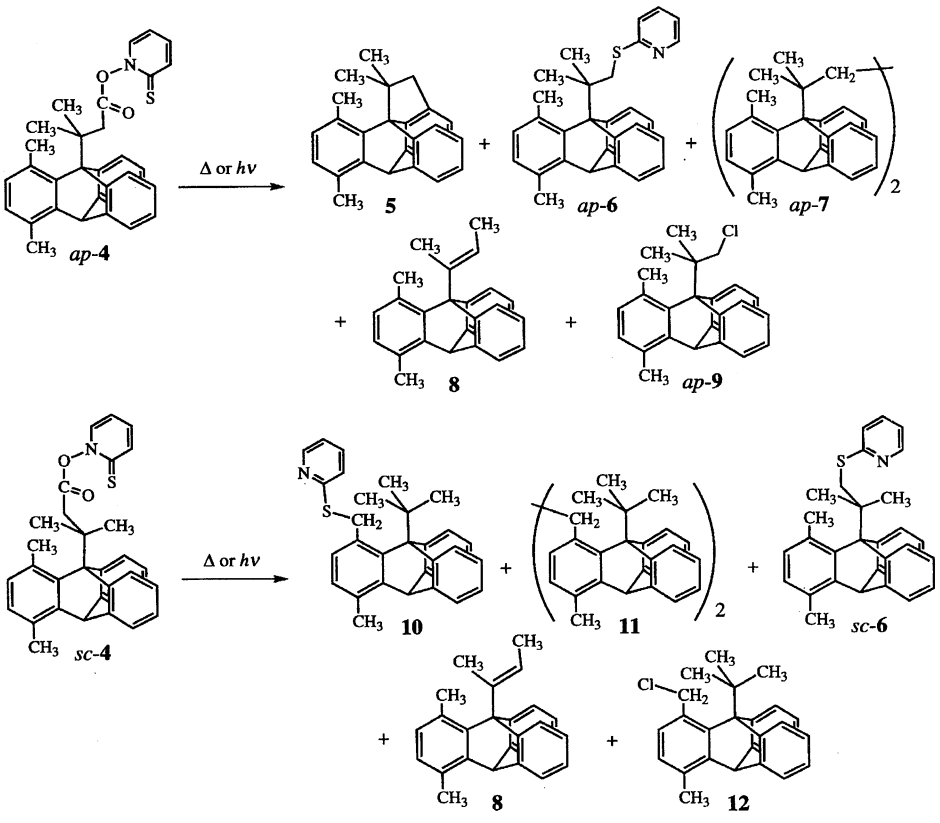
Scheme 2.

These esters are pale yellow crystals and stable in the crystals and solutions at room temperature when protected from light. The crystals of *ap*- and *sc*-**4** decomposed at about 200 and 170 °C, respectively, with evolution of CO_2 gas. These compounds are light sensitive both in the crystals and in solutions: When a solution of the ester in an organic solvent was exposed to indoor light, the decomposition was completed within 30 min with disappearance of yellow color.

UV-vis spectra of the esters could be measured by the method of rapid scanning without significant decomposition. The both compounds have strong absorption at 293.5 and 367.5 nm, the latter band being attributed to the π–π^* transition of the C=S chromophore as mentioned later. No absorptions at wavelengths longer than 450 nm were observed.

Thermolyses. Thermolyses of the rotameric esters were carried out in toluene, benzene, or carbon tetrachloride at a refluxing temperature under an argon atmosphere. In each case, the effect of radical initiator was examined by addition of 10 mol% of azobisisobutyronitrile (AIBN). The decomposition was also performed without solvent at 200 °C under an argon atmosphere.

The course of the decomposition was monitored by TLC or NMR. After the completion of the decomposition, the reaction mixture was analyzed by the ^{1}H NMR spectroscopy. The products obtained from these reactions are shown in Scheme 3, of which structures were determined as described later. The yields of the products in the reactions of *ap*-**4** and *sc*-**4** under various conditions are listed in Tables 1 and 2,



Scheme 3.

Table 1. Product Yields of Thermolyses (Δ) and Photolyses ($h\nu$) of 2(1*H*)-Thioxo-1-pyridyl *ap*-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoate (*ap*-**4**)

Reaction conditions				Products (%)					
Method	Solvent	Temp/°C	Time	**5**	*ap*-**6**	*ap*-**7**	**8**	*ap*-**9**	*ap*-**3**
Δ	Toluene	110	18 h	55	6	0	6	—	19
Δ[a]	Toluene	110	1 h	38	Trace	0	0	—	55
Δ	Benzene	80	48 h	40	3	0	Trace	—	42
Δ[a]	Benzene	80	12 h	59	4	0	Trace	—	23
Δ	CCl_4	80	60 h	25	5	0	Trace	31	25
Δ[a]	CCl_4	80	4 h	34	Trace	0	0	48	12
Δ[b]	No	200	5 min	40	24	0	7	—	20
$h\nu$	Toluene	5	5 min	Trace	58	22	0	—	8
$h\nu$[c]	Toluene	5	5 min	Trace	59	23	0	—	8
$h\nu$	Toluene	110	5 min	32	28	Trace	0	—	14
$h\nu$	Benzene	5	5 min	3	45	33	0	—	9
$h\nu$	CCl_4	5	5 min	0	71	Trace	0	10	10
$h\nu$	No	20	5 min	0	98	0	0	—	0

a) Decomposition was carried out in the presence of 10 mol% of AIBN. b) 9-*t*-Butyl-1,4-dimethyltriptycene was obtained in 4% yield. c) Irradiation through a band-pass filter at 360 nm.

Table 2. Product Yields of Thermolyses (Δ) and Photolyses ($h\nu$) of 2(1*H*)-Thioxo-1-pyridyl *sc*-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoate (*sc*-**4**)

Reaction conditions				Products (%)					
Method	Solvent	Temp/°C	Time	**10**	**11**	*sc*-**6**	**8**	**12**	*sc*-**3**
Δ	Toluene	110	3 h	62	10	0	3	—	13
Δ[a]	Toluene	110	1 h	58	19	0	Trace	—	6
Δ	Benzene	80	18 h	44	3	0	3	—	31
Δ[a]	Benzene	80	6 h	56	6	0	6	—	10
Δ	CCl_4	80	24 h	25	0	0	8	10	36
Δ[a]	CCl_4	80	2 h	48	6	0	0	28	5
Δ	No	200	5 min	75	5	5	Trace	—	7
$h\nu$	Toluene	5	5 min	Trace	56	24	0	—	8
$h\nu$[b]	Toluene	5	5 min	Trace	51	27	0	—	9
$h\nu$	Toluene	110	5 min	6	62	10	0	—	8
$h\nu$	Benzene	5	5 min	Trace	61	20	0	—	5
$h\nu$	CCl_4	5	5 min	Trace	31	49	0	0	9
$h\nu$	No	20	5 min	0	0	90	0	—	3

a) Decomposition was carried out in the presence of 10 mol% of AIBN. b) Irradiation through a band-pass filter at 360 nm.

respectively, together with the reaction times.

***ap*-4.** Thermolysis of the *ap*-ester in toluene was completed after 18 h at the refluxing temperature. This reaction time is much longer than those of an ester having a simple primary alkyl group, where the reaction finishes in a few hours in refluxing toluene.[7]

The thermolysis in toluene gave the cyclized compound (**5**) as a main product, which had been also a major product in the chlorodecarboxylation[4] of the *ap* form, together with *ap*-**6** and **8** in small amounts. The carboxylic acid (*ap*-**3**) was recovered in 19% yield for the reaction in toluene, the recovery being much lower than the case of the Hunsdiecker reaction with lead(IV) acetate.

The decomposition in benzene required longer time than in toluene because of the low reaction temperature. The distribution of the products in benzene is quite similar to that in toluene though the ratio of the recovery of the carboxylic acid is somewhat high and only a trace of **8** was detected.

The reaction in carbon tetrachloride afforded a chloro derivative (*ap*-**9**) in addition to **5** and *ap*-**3** which are common for other reactions.

Thermolysis without solvent was complete after 5 min at 200 °C with evolution of CO_2 gas. The main product is again the cyclized compound (**5**), while the yield of the sulfide (*ap*-**6**) is significantly higher than those in the solutions. A small amount of 9-*t*-butyl-1,4-dimethyltriptycene and the olefin (**8**) were also detected.

Addition of a catalytic amount of AIBN remarkably enhanced the reaction rates as can be seen from the reaction times in Table 1. In toluene, the yield of the carboxylic acid (*ap*-**3**) increased at the expense of compound **5**, while compound **5** increased in its yield at the expense of that of the carboxylic acid in benzene and carbon tetrachloride. The yield of *ap*-**9** also significantly increased when AIBN was

added to carbon tetrachloride solutions. Addition of AIBN seems to reduce the yield of the olefin (**8**).

***sc*-4.** The *sc*-ester decomposed much faster than the *ap* ester in toluene at the refluxing temperature, whereas the enhancement of the reaction rates was diminished in benzene and carbon tetrachloride.

The thermolysis in benzene or toluene gave compound **10**, having a *t*-butyl group at the 9-position and a 2-pyridylthio group at the 1-methyl group, as a major product and the dimeric compound **11** in ca. 10% yield. The yield of the carboxylic acid (*sc*-**3**) was significantly higher for the reaction in benzene than that in toluene. No unrearranged products such as *sc*-**6** were observed under the conditions. The thermolysis of *sc*-**4** never produced the cyclized compound (**5**), which had been the major product from the *ap*-ester. The olefin (**8**) was also detected in small amounts.

The reaction of *sc*-**4** in carbon tetrachloride gave the 1-chloromethyl compound **12** in a moderate yield together with **10**. We could not here find even a trace of a chloro compound derived from the unrearranged radical. It is also noted that the yield of the carboxylic acid is significantly increased in this solvent relative to that for toluene solvent.

Thermolysis without solvent at 200 °C afforded **10** as a major product in addition to the dimer **11**. It is noted that an unrearranged product *sc*-**6** was present among the products, although the yield was low.

Addition of AIBN caused the decrease in the yields of *sc*-**3**, whereas the yields of compound **11** slightly increased. The rate enhancing effects of AIBN were marked in carbon tetrachloride whereas those in toluene and benzene were moderate. The yields of compound **10** were increased in benzene and carbon tetrachloride, whereas that was reduced in the reaction in toluene, when compared with the reactions without AIBN. The presence of AIBN seems to reduce the yield of compound **8**, although there is one exception.

Photolyses. These were carried out with a high-pressure mercury lamp with a glass filter, unless otherwise mentioned, in the same solvents used for the thermolysis, the solutions being degassed before use. The reaction temperatures were generally kept at about 5 °C to avoid a thermal reaction. The decomposition was also accomplished by the direct irradiation of the esters at the solid state at room temperature. The reactions were rapid and complete within 5 min. The common feature in photolyses is the absence of the olefin (**8**) in any case. The results are shown in Tables 1 and 2, and the products in Scheme 3.

***ap*-4.** The product distributions in the photolysis of *ap*-**4** are quite different from those in the thermolysis. The reactions in toluene and benzene gave very low yields of the cyclized compound **5**, while the *ap*-sulfide (*ap*-**6**) and the dimeric compound (*ap*-**7**) were dominant products. It deserves mention that *ap*-**7** was never produced in the thermolysis. Irradiation of a carbon tetrachloride solution did not afford compound **5** but the *ap*-sulfide (*ap*-**6**) in 71% yield and a small amount of the chloride *ap*-**9**.

The *ap*-ester was readily decomposed by irradiation of the crystals within a few minutes. The feature of the result is that *ap*-**6** was an exclusive product. No other products which were observed in other reactions were detected.

The results of the photolysis at 110 °C in toluene indicate that, while the yield of *ap*-**7** decreased considerably, that of **5** increased substantially, relative to the results at 5 °C. The yield of the carboxylic acid increased also.

***sc*-4.** The photolyses of the *sc*-ester in solutions mainly produced the dimer (**11**) together with the *sc*-sulfide (*sc*-**6**), the ratio of the two being dependent on the solvent. In contrast to the thermolysis, the sulfide (**10**) was obtained only in a trace amount in all solvents examined. The yields of the carboxylic acid (*sc*-**3**) were generally low.

The photolysis of the solid *sc*-ester gave the *sc*-sulfide (*sc*-**6**) predominantly together with a small amount of the carboxylic acid. No rearranged products such as **11** or **12** were detected.

The feature in the photolysis at 110 °C in toluene is the increase in the yield of **10**. The yield of **11** increased, whereas that of *sc*-**6** decreased, but the effects of the temperature were moderate.

Identification of the Products. Because compounds **5**, **8**, *ap*-**9**, and **12** have already been identified or independently synthesized in our previous works,[4,13,14] these compounds in the products were characterized by comparing their ^{1}H NMR with authentic samples.

^{1}H NMR spectroscopic data indicate that compound **6** has a 2-pyridylthio group in the *t*-alkyl group at the 9-position. The methylene protons attached to the sulfur atom appeared as a singlet and an AB quartet for the sulfides obtained from the *ap* and *sc* esters, respectively, suggesting that the sulfides had the same stereochemistries as the original esters. When *ap*-**6** was heated at 200 °C for 12 h, a mixture of *ap*-**6** and *sc*-**6** in ca. 1 : 1 ratio was obtained. This isomerization test clearly shows that the two compounds are rotational isomers with each other.

Compound **10** also has a 2-pyridylthio group and shows a similar ^{1}H NMR pattern as *ap*-**6**. We expected that **10** had the substituent at the 1-methyl group from a large difference in the chemical shifts of the 2- and 3-protons. The structure of **10** was finally confirmed by the independent synthesis: The reaction of the chloride **12** with sodium 2-pyridinethiolate produced the same compound. Therefore, **10** has a 2-pyridylthiomethyl group at the 1-position and a *t*-butyl group at the 9-position.

Compounds *ap*-**7** and **11** are hydrocarbons with the same molecular formula, which do not melt even at 350 °C. The mass analysis showed that they had two triptycene moieties in a molecule. Therefore, each compound should have a dimeric structure shown in Scheme 3.

9-*t*-Butyl-1,4-dimethyltriptycene was independently synthesized from 9-*t*-butylanthracene and 3,6-dimethylbenzyne which was produced in situ from 3,6-dimethylanthranilic acid and isopentyl nitrite. Comparison of the NMR spectra confirmed the structure of the compound in the products.

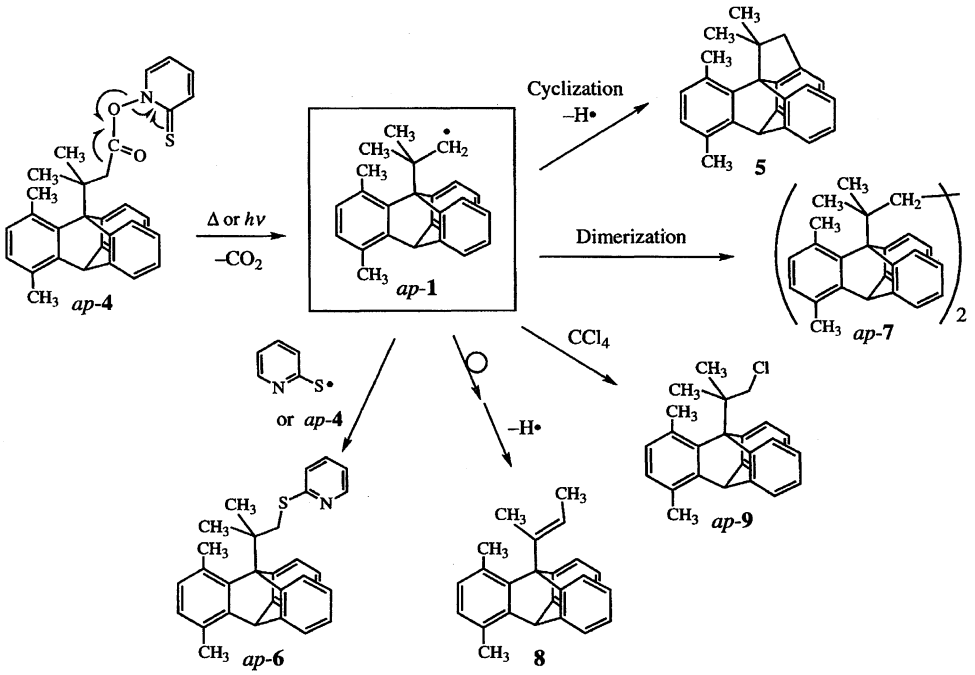
Not shown in Tables 1 and 2 are di(2-pyridyl) disulfide for the thermolysis in hydrocarbon solvents and 2-pyridyl trichloromethyl sulfide[8] for the thermolysis in carbon tetra-

chloride. These sulfides are known compounds.

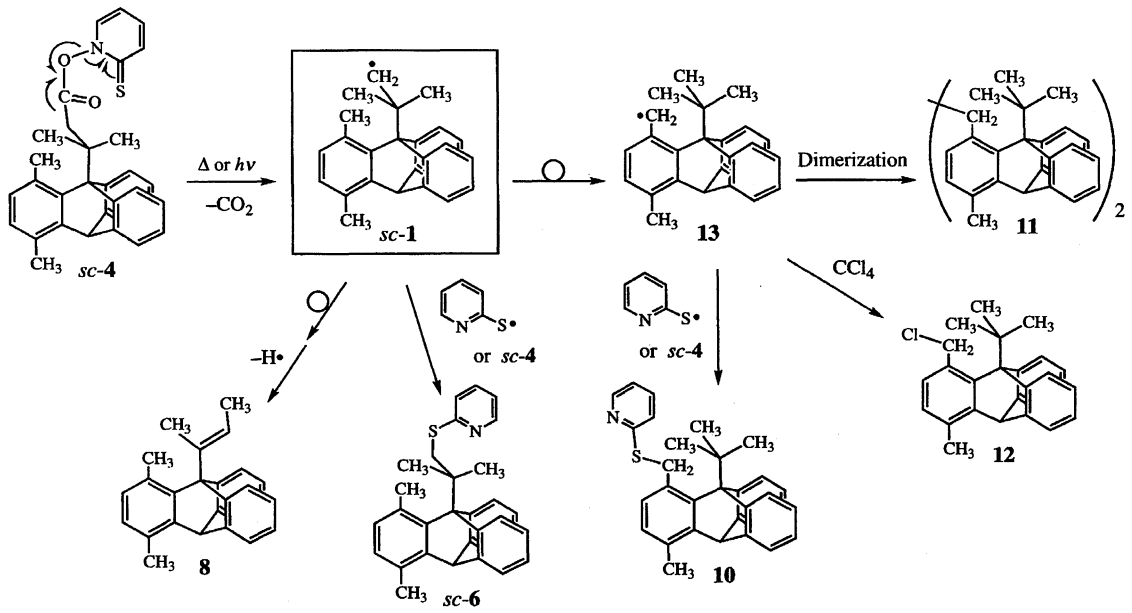
Discussion

General Considerations. The mechanisms of the reaction were discussed in some detail by Barton et al.[15] Their main postulate is that an alkyl radical which is very easily formed by decarboxylation of the alkylcarboxyl radical derived by the N–O bond scission adds to a C=S bond of another 2(1*H*)-thioxo-1-pyridyl ester molecule to induce decomposition but this addition is reversible.[16] Thus it is an induced decomposition of a chain nature and the 2-pyridylthioalkane is the main product if there is no good radical trap.[17] We feel this is an oversimplified picture of the reaction mechanisms because they neglect the cage effect which is important when the solution is viscous. Especially because we have found that the reaction in solid phase produces exclusively the 2-pyridylthioalkane, recombination of the alkyl radical with the 2-pyridylthio radical or addition of the alkyl radical to the C=S bond of 2(1*H*)-thioxo-1-pyridyl radical in cage must be taken into consideration. We discuss the results in the light of these considerations.

Schemes 4 and 5 show possible reaction pathways to products from *ap*-**4** and *sc*-**4**, respectively, in which the initial step is the homolytic cleavage of the O–N bond followed by loss



Scheme 4.



Scheme 5.

of carbon dioxide from the carboxyl radical to give the primary radical **1**. The two radicals, 2-pyridylthio and 2-(1,4-dimethyl-9-triptycyl)-2-methylpropyl (**1**), and carbon dioxide are encaged in the initial state but carbon dioxide is lost from the cage soon after the formation. In the cage, the geminate radicals can recombine to form *ap*-**6** or *sc*-**6**. However, the radical **1** can follow another fate, namely the intramolecular reaction with the benzene ring which is in its vicinity. This reaction will lead to **5**. If the radical rearranges in some ways, the reaction leads to the formation of **8**. *ap*-**3** (*sc*-**3**) and *ap*-**6** (*sc*-**6**) may be formed in the cage or out-of-cage but *ap*-**7** is clearly the out-of-cage product.

Our previous works have shown that **5** could be produced in the cation-forming reaction at the same position as the radical center of *ap*-**1**.[5] However, the cation pathway can be ruled out for the following reasons. If the cation were a main intermediate in the reaction, products derived from the rearranged tertiary cation, i.e. olefin **8**, should be obtained more abundantly. In practice, however, the yields of such compounds are very low compared to the cyclized compound (**5**). In the literature it is reported that a Wagner–Meerwein type rearrangement is never observed in the thermolysis of 2-thioxopyridyl ester of 3,3-dimethylbutanoic acid.[8] These experimental results mean that the reactive intermediate generated by the method is far from cationic but a typical radical. Therefore, the main product, the cyclized compound (**5**), is produced by the simple radical aromatic substitution to one of the peri-carbons of the nonsubstituted benzeno groups followed by hydrogen abstraction.

The formation of a small amount of the olefin (**8**) means that rearrangement of the alkyl group at the 9-position takes place during the reaction as a minor route. This kind of rearrangement is popular for the cation reaction,[5] and rationalization is easy if any oxidizing condition is present. Although there are examples of 1,2-rearrangement of alkyl groups in carbon radicals,[18] migration of an alkyl radical is known to be very slow. The notable examples are confined to the migration of aryl groups, cases of the neophyl type rearrangement being typical.[19] In addition, it is known that neopentyl type radicals do not rearrange appreciably under normal conditions.[20] However, the release from the congested state by rearrangement can be a motive force for the rearrangement. There is also a possibility that the homolysis of the ester takes place by charge separation as was postulated by Walling et al.[21] If this kind of fission takes place, the rearrangement should be facile. It is difficult to rule out any of these possibilities.

In all cases, considerable amounts of carboxylic acids (*ap*-**3** and *sc*-**3**) were obtained. This is quite different from what reported by Barton et al., the carboxylic acids being little formed if the carboxylic acid is aliphatic. However, because diacyl peroxide[22,23] or *t*-butyl peroxyacetate[24] as well as dibenzoyl peroxide[25–27] is known to produce acyloxyl radical at the initial step of thermolyses and the produced acyloxyl radical behaves in nearly the same manner, if not the same, the thioxopyridyl ester will also follow the same paths as these peroxy compounds after generating the acyloxyl radical. The high yields of the acids are noteworthy but are very often encountered in other thermolyses of diacyl peroxides. It is interesting to note that 9-*t*-butyl-1,4-dimethyltriptycene, which should be formed by hydrogen abstraction by the radical *ap*-**1**, *sc*-**1** or **13**, is not formed in toluene.

The formation of chloro compounds (*ap*-**9** and **12**) in the reactions in carbon tetrachloride is due to chlorine abstraction by radicals *ap*-**1** or **13**. Because carbon tetrachloride is known to be a moderately good radical trap, the results agree with those published. The dimers (*ap*-**7** and **11**) are out-of-cage products. Because of the rapid hydrogen transfer from the 1-methyl group to the radical center in *sc*-**1**, no *sc*-9-(2-chloro-1,1-dimethylethyl)-1,4-dimethyltriptycene was found in the product. The ample formation of the dimer **11** may be attributed to the stability of **13**, thanks to the benzylic nature as well as steric protection. That is, it can migrate out-of-cage without reacting with other species.

Comparison of Reactivities of and Products from *ap*-4 and *sc*-4 in Thermolyses in Toluene. The high stability of *ap*-**4** relative to *sc*-**4** may be attributed to the steric effect of the triptycene moiety. This rate enhancement in the *sc*-form must be explained by the steric acceleration. However, steric effects alone cannot explain the abnormal stability of *ap*-**4** toward heat.

The outstanding difference in the products between the thermolyses of the rotamers in toluene is that *ap*-**4** gives those which can be explained from the produced radical (*ap*-**1**) directly except the olefin **8**, whereas *sc*-**4** gives rearranged products except for the carboxylic acid (*sc*-**3**). The formation of **10** as a main product from *sc*-**4** is the feature of the results. Namely, the *ap*-isomer reacts mostly in-cage to afford compounds **5** and **8**. *ap*-**6** may be the product of both in-cage and out-of-cage, whereas the carboxylic acid (*ap*-**3**) is possibly an out-of-cage product. By contrast, *sc*-**4** gives 9-*t*-butyl-4-methyl-1-[(2-pyridylthio)methyl]triptycene (**10**) together with a dimer, 1,2-bis(9-*t*-butyl-4-methyl-1-triptycyl)ethane (**11**), and *sc*-**3**. The facile hydrogen transfer from the 1-methyl group to the radical site in *sc*-**1** is feasible because the benzylic radicals are known much more stable than normal alkyl radicals and these two sites are located very closely. From the X-ray structures of related compounds, the nonbonding distances from the radical carbon to the 1-methyl carbon are found to be only 3.1 Å,[28–30] apparently shorter than the sum of van der Waals radii of a hydrogen and a methyl group (ca. 3.60 Å).[31] This type of facile hydrogen migration had been also observed in the chlorodecarboxylation of the *sc*-carboxylic acid with the use of lead(IV) acetate.[4]

Although the carboxylic acid may be classified as an out-of-cage product, it is actually a product which is formed by the reaction of the radical with the wall of cage or even by the reaction of the acyloxyl radical with the species in the cage. Therefore the true out-of-cage products are the dimer, *ap*-**7** and **11**, the former of which was not detected from *ap*-**4**. This must be due to the stability of the benzylic radical **13** which has long enough life time to escape from the cage and to recombine. By contrast, the life time of *ap*-**1** radical is short and either it recombines with 2-pyridylthio radical

in the cage or adds to another molecule of *ap*-**4**, which is in another cage, to afford *ap*-**6**. It has no chance of producing the dimer *ap*-**7** because of low concentration.

A compound of *ap*-**6** type, which is produced either by recombination of *ap*-**1** with the 2-pyridylthio radical or by addition of *ap*-**1** to the C=S bond of another molecule of *ap*-**4**, is known as an almost exclusive product in thermolyses of the thioxopyridyl esters if a good radical trap is absent.[8] However, the yield of *ap*-**6** is only 6% here. The low yield of *ap*-**6** is attributed to the steric effect of the triptycene moiety. The carbon where the radical is generated is expected to be pushed into the notch between the two nonsubstituted benzene rings in order to avoid the steric interaction of 9-alkyl group with the 1-methyl group, as evidenced by the X-ray structures of the related compounds.[13,28–30] This crowded situation prevents the carbon radical from coupling with a thio radical (or addition to the C=S bond) and the carbon radical attacks one of the peri-carbons at a proximate position of the benzene bridges. However, addition of a radical to a benzene ring is known to be a slow process.[32] Thus the reaction competes with others.

While the cyclic compound **5** is the major product from *ap*-**4**, major is 9-*t*-butyl-4-methyl-1-[(2-pyridylthio)methyl]-triptycene **10** from *sc*-**4**. The results are attributed to facile hydrogen migration from the 1-methyl group to the radical site in *sc*-**1**. Since the radical site in *sc*-**1** is pushed out of the triptycene skeleton with respect to the *ap*-methyl, the formation of *sc*-**6** will suffer from less steric hindrance than that of *ap*-**6**. Yet, *sc*-**6** is congested around the 9-substituent and hydrogen migration is rapid to form the stable radical **13** which can react with the thio radical to form **10**. In this case, addition of the radical to the C=S bond of another *sc*-**4** molecule is less likely because of the steric effect.

The structure of *ap*-**1** discussed above is also responsible to the high yield of the cyclized compound **5**. Because the radical center is close to one of the unsubstituted benzene bridges, the radical interacts easily with the π^* orbital of the benzene ring to afford an adduct which is then dehydrogenated to give **5**. By contrast, the radical center in *sc*-**1** is located rather distantly from the unsubstituted benzene rings for the same reasons, the hydrogen migration being preferred to the cyclization to yield **5**.

Addition of AIBN should cause induced decomposition of the thioxopyridyl ester. In accordance with this statement, the reaction is accelerated to a considerable degree when AIBN was added. Addition of the radical from AIBN to the C=S bond produces the carboxyl radical exclusively from *ap*-**4** and the geminate thio radical is absent in the initial decomposition. Thus the yield of the carboxylic acid (*ap*-**3**) was increased whereas that of *ap*-**6** decreased. The decrease in the yield of **8** is not well understood at the moment. In contrast, the product distribution from *sc*-**4** is not affected significantly by addition of AIBN except for the increase in the yield of the dimer **11**. The increase in **11** can also be interpreted by selective formation of the carboxyl radical from *sc*-**4**, although there are some points which need further investigation.

Solvent and Phase Effects on Product Distribution. Effects of solvent viscosity are often invoked in discussing the products of radical reactions because the ease of escape from the cage is thought to be dependent on the viscosity. Toluene and benzene possess so similar viscosity that the viscosity effects may be insignificant in discussing the product distribution.

In benzene, *ap*-**4** gave similar results with those in toluene, although some decreases in the yields of **5** and **8** and the increase in that of *ap*-**3** were noted. We wish to attribute these results to the effects of temperature. Cyclization to form **5** needs some activation energy as is mentioned above. Rearrangement to produce **8** also needs activation energy as implicated in the cation case.[5] Therefore yields of these compounds should decrease at low temperatures and the out-of-cage reaction should increase. However, the dimer *ap*-**7** was not detected in benzene.

When carbon tetrachloride is used as a solvent, chlorine abstraction by the radicals from the solvent takes place to a considerable degree to afford *ap*-**9** or **12**: A modern version of Hunsdiecker chlorodecarboxylation[7–9] takes place. When these products are formed, the amounts of compound **5** in the case of *ap* and that of compound **10** in the case of *sc* diminished, indicating that the chlorine abstraction and intramolecular radical attack on the benzene ring in the *ap*-case or colligation in the *sc* compete because carbon tetrachloride is a moderately efficient radical trap. The relative rates of hydrogen and chlorine abstraction are discussed and generally chlorine abstraction from carbon tetrachloride is preferred to hydrogen abstraction from toluene.[33] The results are in conformity with those in the literature in the case of *ap*-**4**. It is interesting to note that the main product is not a chlorine-abstraction product but the thio ether in the *sc*. This will mean that the steric effects are important, because a sulfur radical or atom is smaller than a chlorine atom.

Addition of a catalytic amount of AIBN to the carbon tetrachloride solution increased the yields of the chlorides *ap*-**9** and **12** as well as the reaction rate, whereas the yields of the carboxylic acids were diminished. The results are again attributed to the preferential formation of the carboxyl radical and absence of a geminate thio radical in initial induced decomposition.

Thermolysis of the melts of the thioxopyridyl esters at 200 °C gave an appreciably high yield of *ap*-**6** in the case of *ap*-**4** and it deserves mention that *sc*-**6**, the recombination product of the initially formed radical (*sc*-**1**) with 2-pyridylthio radical, was detected among the products from *sc*-**4**, though the yield was rather low. The increase in the yield of *ap*-**6** should be attributed to the high temperature, where the reaction becomes competitive with the cyclization to form **5**. Formation of the unrearranged compound (*sc*-**6**) means that the rearrangement of *sc*-**1** to **13** requires an activation energy even though the energy barrier is expected to be very low. Because the motion of the molecules is strongly restricted in the melts, the thio radical can couple with the unrearranged radical without moving away from the original positions.

The thermolysis of *ap*-**4** at 200 °C without solvent pro-

duced a small amount of 9-*t*-butyl-1,4-dimethyltriptycene, of which formation is explained by hydrogen abstraction by *ap*-**1**. We attribute the results to the increase in the chance of hydrogen abstraction at a high temperature for *ap*-**1** because other main reactions forming **5** and *ap*-**6** require some activation energy. Absence of 9-*t*-butyl-1,4-dimethyltriptycene among the products from *sc*-**1** is attributed to the presence of other facile ways of reacting.

Comparison of the Results of Thermolyses with Those of Photolyses. Photolyses[34,35] of dibenzoyl peroxide and other diacyl peroxides are well documented. Since decomposition of both *t*-butyl peroxybenzoate[24] and *N*-benzoyl-*N*-nitroso-*O*-*t*-butylhydroxylamine[36] produces benzoyloxyl radical, which further decomposes to give similar product ratios, we again use the reactivities of these well known radical sources as references in discussing the results obtained here.

Photolysis of dibenzoyl peroxide as well as that of *t*-butyl peroxybenzoate[37] gives very similar results with those of the corresponding thermolyses. This is because photolyses of these compounds proceed usually via singlet radical pairs.[35,38] If a triplet sensitizer was added to the system of photolyses, the kinetics as well as products are significantly different.[39,40] The outstanding difference between thermolyses and photolyses of 2(1*H*)-thioxo-1-pyridyl esters is the formation of the dimer from the intervening radicals in the latter[15] and this feature is reproduced in the present work. If the multiplicity of the intervening radicals are different in thermolyses and in photolyses, the products could be different as well. Therefore the electronic state deserves consideration.

Thiones are known to be photolyzed by two mechanisms:[41] By excitation to S_1 (n–π^*) followed by intersystem crossing to T_1 and by excitation to S_2 (π–π^*). Since the former reaction proceeds through a triplet state, the difference between the thermolyses and photolyses may be attributed to this difference in mechanisms. Photolyses of thiones with light of long wave length (>450 nm) are known to proceed via the n–π^* triplet state.[42—45] The products missing in this operation, which are found when shorter wavelength light is used, are concluded to be those derived via the singlet state.

The UV-vis spectra of the thioxopyridyl esters were not self-evident, because no absorption was observed at longer wave lengths than 450 nm, which should be attributed to the n–π^* transition to lead to T_1. Instead, the compounds showed strong absorptions with maxima at 294 and 368 nm, the assignment of which was made by calculation.

Calculation by CINDO/S[46] of a model compound, 2(1*H*)-thioxo-1-pyridyl acetate, showed that it should possess absorptions at 345 and 285 nm, both of which should be attributed to π–π^* transition, a weak absorption at 289 nm attributable to n–π^* transition of the carbonyl group and a very weak one at 579 nm which is due to n–π^* transition of the C=S moiety.

These results indicate that the ordinary photolyses with irradiation with a high-pressure mercury lamp through a Pyrex glass filter might proceed via absorption of electromagnetic waves of three wavelengths. In order to shed light on the effects of the wavelength of exciting light, we adopted methods of photolyses with other filters.

Photolyses with a filter which permits transmission of light of >450 nm wavelength did not cause any detectable change at 5 °C after 2 h. The light of this long wavelength region does not seem to effect photolysis of the compounds, probably because the absorption is too weak. With even this information, there is a possibility that the photolysis of the compounds proceeded by the light of nearly 300 nm wavelength but not by the 368 nm light, because the absorption with the maximum at 294 nm (285 or 289 nm by calculation) should extend to this region and indeed there is a report in the literature that the esters were photolyzed easily with 308 nm laser light.[47]

Then we performed photolysis with 360 nm light. The reaction time and the product distributions were hardly influenced by the use of this band-pass filter for the both esters, as are shown in Tables 1 and 2.[48] The result suggests that the photolysis proceeds via an S_2 state by π–π^* excitation of the conjugated C=S moiety. Photolysis by the 308 nm light may well be taken as via an S_3 state by π–π^* excitation of the C=S moiety, because the n–π^* absorption of the C=O is very weak. Thus practically all the photolyses proceed via singlet states.

We wish to explain the drastic change in the reactivities from thermolysis to photolysis in the following ways. The unfavorable formation of compound **5** from *ap*-**1** in photolysis indicates that the addition of the radical center to the aromatic ring is a more energy-requiring process than normal addition of radicals to a benzene ring.[49] It is reasonable because the cyclized structure with a condensed five-membered ring has serious strain as evidenced by the X-ray and molecular mechanics studies.[13] Molecules cannot obtain internal energy high enough for the cyclization under the conditions since the photolytic reactions were generally carried out at low temperatures compared with the thermolysis. It is also true that photolyses provide much higher concentration of radicals in the system than thermolyses. Thus the coupling of the carbon radical with other radicals becomes a preferred process in the photolysis.

In fact, photolysis at 110 °C in toluene showed higher yields of the cyclized compound **5** at the expense of *ap*-**6** and *ap*-**7**. It might be argued that the reaction at 110 °C should be affected by thermolysis. However, because the thermolysis is a slow reaction as indicated by the reaction time for completion (Tables 1 and 2) and photolysis is completed within 5 min, the effects of thermolyses may be neglected.

Facile photo-induced decomposition as well as the low reaction temperature generates the radicals in relatively high concentration in the solution. The carbon radical has more chances to encounter another carbon radical, when it escapes from the cage, even though carbon radicals are less stable than sulfur radicals. Thus formation of the dimer *ap*-**7** is observed, differing from the results of thermolyses. From the thermodynamic viewpoint, the formation of a C–C bond is preferred to that of a C–S bond. Due to the high stability

of the radical **13**, photolysis of *sc*-**4** in toluene or benzene yields the dimer **11** as the main product.

Photolysis of *ap*-**4** in carbon tetrachloride gave *ap*-**6** as a main product, while it gave the chlorine abstraction product in 10% yield. The negligible formation of the dimer *ap*-**7** may be attributed to the high viscosity of CCl_4, in which the escape of the carbon radicals from the cage is restricted. The formation of *ap*-**6** in high yields suggests that radical recombination in the cage is a dominant process. By contrast, *sc*-**4** afforded the dimer **11** in a fairly high yield, while the chloro compound **12** was not detected. We attribute the results again to the stability of the radical **13**. The chlorine abstraction is an energy requiring process and will be slow at a low temperature, as was discussed for the thermolysis of *ap*-**4**, whereas recombination of radicals will need little energy for completion. In addition, the radical **13** has ample chances of escape from the cage due to its stability.

Another feature of the photolysis is the formation of the unrearranged product *sc*-**6** in moderate yields. This again supports the idea that the hydrogen migration requires an activation energy as discussed in the thermolysis in the absence of solvent. The low reaction temperature of the photolysis allows *sc*-**1** to survive for a longer time than the case of the thermolysis to couple with a thio radical before rearrangement. The coupling of the unrearranged radicals seems to be an unfavorable process due to the steric effect as has been discussed.

The mechanistic explanation for the reaction in the crystals is easy. In the solid state, the mobility of molecules is extremely restricted compared with that in solution. Therefore, the alkyl radical cannot move out of the lattice but couple with the thio radical generated at the same site. The hydrogen transfer from the 1-methyl to the radical center in *sc*-**1**, which is a dominant course of the *sc*-radical for the thermolysis as well as for the photolysis in solutions, does not take place under the conditions. The selective reaction is attributed to the extremely restricted motions of the generated radicals.

Experimental

Melting points are uncorrected. ^{1}H NMR spectra were measured by a Varian Gemini-300 or a JEOL GSX-400 spectrometer operating at 300.1 and 399.8 MHz, respectively. Mass spectra were measured on a JEOL JMS-DX303 spectrometer. Elemental analyses were performed by a Perkin–Elmer 240C analyzer.

2(1*H*)-Thioxo-1-pyridyl *ap*-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoate (*ap*-4). *ap*-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoyl chloride, prepared from 500 mg (1.31 mmol) of the corresponding acid[10] and 1.14 mL (13.1 mmol) of oxalyl dichloride, was dissolved in 20 mL of dry THF in a flask shielded from light with aluminium foil under an argon atmosphere. To the solution were added 246 mg (1.57 mmol) of 2-mercaptopyridine 1-oxide sodium salt (Fluka Fine Chemicals) and 16 mg (0.13 mmol) of 4-(dimethylamino)pyridine. The reaction mixture was stirred overnight at room temperature. Following workup and purification were performed under the dimmed light. The solution was filtered with a glass filter and the filtrate was evaporated under a reduced pressure. The residue was chromatographed on silica gel eluted with dichloromethane and recrystallization of the main fraction gave 470 mg (73%) of the desired compound as pale yellow crystals. Mp 195—200 °C (decomp with foaming). Found: C, 77.84; H, 5.83; N, 2.85%. Calcd for $C_{32}H_{29}NO_2S$: C, 78.18; H, 5.95; N, 2.85%. ^{1}H NMR ($CDCl_3$) δ = 2.50 (9H, s), 2.67 (3H, s), 4.10 (2H, s), 5.61 (1H, s), 6.66 (1H, dt, J = 1.9 and 7.0 Hz), 6.76 (2H, s), 7.00—7.10 (4H, m), 7.23 (1H, ddd, J = 8.8, 7.0, and 1.6 Hz), 7.41 (2H, m), 7.68 (1H, dd, J = 7.0 and 1.6 Hz), 7.76 (1H, dd, J = 8.8 and 1.6 Hz), 7.92 (2H, m). UV ($CHCl_3$) 293.5 (log ε 4.3), 367.5 nm (3.9).

2(1*H*)-Thioxo-1-pyridyl *sc*-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoate (*sc*-4). This compound was similarly prepared from *sc*-3-(1,4-dimethyl-9-triptycyl)-3-methylbutanoic acid in 47% yield. Mp 170—174 °C (decomp with foaming). Found: C, 78.04; H, 5.82; N, 2.80%. Calcd for $C_{32}H_{29}NO_2S$: C, 78.18; H, 5.95; N, 2.85%. ^{1}H NMR ($CDCl_3$) δ = 2.37 (3H, s), 2.44 (3H, s), 2.54 (3H, s), 2.81 (3H, s), 4.15 and 4.35 (2H, ABq, J = 17.9 Hz), 5.61 (1H, s), 6.67 (1H, dt, J = 1.8 and 6.9 Hz), 6.81 (2H, s), 6.97—7.07 (4H, m), 7.24 (1H, ddd, J = 8.8, 7.1, and 1.4 Hz), 7.34—7.42 (2H, m), 7.67 (1H, dd, J = 6.9 and 1.4 Hz), 7.76 (1H, dd, J = 8.8 and 1.8 Hz), 7.84 (1H, m), 7.92 (1H, m). UV ($CHCl_3$) 293.5 (log ε 4.3), 367.5 nm (3.9).

Thermolysis of the Esters. An ester (20 mg or 0.041 mmol) was dissolved in about 4 mL of an appropriate solvent, which was purified in an ordinary manner. If necessary, 0.1 molar amount of AIBN was added to the solution. This solution was degassed by the use of a technique of freeze-thaw, and refluxed under an argon atmosphere in the dark. The heating was continued until a TLC spot due to the starting ester became undetectable. After the solvent was evaporated, the residue was separated by a preparative TLC (Merck, 2mm) eluted with 1 : 1 hexane–dichloromethane. Yields of the products were read from integral intensities of ^{1}H NMR as well as weight analysis of the separated products.

Photolysis of the Esters. A solution similarly prepared as the thermolysis was placed in a cool water (ca. 5 °C) unless otherwise mentioned. The solution was irradiated with a 100 W high-pressure mercury lamp for 5 min through a Pyrex glass as a cut-off filter. If necessary, the sample was irradiated though a cut-off filter at shorter wavelength than 450 nm (Toshiba Y-45) or a band-pass filter around 360 nm (UV-D36C). The reaction was usually completed within 1 min as judged from the disappearance of yellow color of the solution. The solvent was evaporated and the residue was similarly analyzed.

Identification of Products. 1,1,7,10-Tetramethyl-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthracene (**5**),[13] 1,4-dimethyl-9-[(*E*)-1-methyl-1-propenyl]triptycene (**8**),[14] *ap*-9-(2-chloro-1,1-dimethylethyl)-1,4-dimethyltriptycene (*ap*-**9**), and 9-*t*-butyl-1-chloromethyl-4-methyltriptycene (**12**)[4] were known compounds. Di(2-pyridyl) disulfide was commercially available from Aldlich Chemical Co. Analytical data of 2-pyridyl trichloromethyl sulfide were reported in the literature.[8]

9-*t*-Butyl-1,4-dimethyltriptycene was prepared from 9-*t*-butylanthracene[49] and benzyne by a standard method. Mp 229.0—230.0 °C. Found: C, 92.33; H, 7.88%. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74%. ^{1}H NMR ($CDCl_3$) δ = 2.07 (3H, s), 2.24 (6H, s), 2.50 (3H, s), 2.66 (3H, s), 5.58 (1H, s), 6.74 (2H, s), 6.93—7.01 (4H, m), 7.35 (2H, m), 7.88 (2H, m).

***ap*-1,4-Dimethyl-9-[2-(2-pyridylthio)-1,1-dimethylethyl]-triptycene (*ap*-6).** Mp 212—215 °C. Found: C, 82.99; H, 6.54; N, 2.92%. Calcd for $C_{31}H_{29}NS$: C, 83.18; H, 6.53; N, 3.13%. ^{1}H NMR ($CDCl_3$) δ = 2.34 (6H, s), 2.50 (3H, s), 2.63 (3H, s), 4.63 (2H, s), 5.60 (1H, s), 6.74 (2H, s), 6.95—7.07 (5H, m), 7.28 (1H, dt, J = 8.1 and 1.0 Hz), 7.38 (2H, m), 7.48 (1H, dt, J = 1.8 and 7.7 Hz), 8.15 (2H, m), 8.45 (1H, dq, J = 5.2 and 1.0 Hz). When this

compound was heated in a refluxing tetralin solution for 12 h, a 1 : 1 mixture of *ap* and *sc* isomers was obtained.

***sc*-1,4-Dimethyl-9-[2-(2-pyridylthio)-1,1-dimethylethyl]-triptycene (*sc*-6).** Mp 172.0—175.0 °C. Found: C, 83.34; H, 6.66; N, 2.84%. Calcd for $C_{31}H_{29}NS$: C, 83.18; H, 6.53; N, 3.13%. ^{1}H NMR ($CDCl_3$) δ = 2.16 (3H, s), 2.28 (3H, s), 2.54 (3H, s), 2.68 (3H, s), 4.22 and 5.19 (2H, ABq, J = 14.2 Hz), 5.60 (1H, s), 6.78 (2H, s), 6.94—7.09 (5H, m), 7.29 (1H, d, J = 9.1 Hz), 7.37 (2H, m), 7.49 (1H, dt, J = 1.9 and 7.9 Hz), 7.85 (1H, m), 8.32 (1H, d, J = 7.1 Hz), 8.44 (1H, app. d, J = 4.9 Hz).

2,5-Dimethyl-2,5-bis[*ap*-(1,4-dimethyl-9-triptycyl)]hexane (*ap*-7). Mp 355—363 °C (decomp). An analytical sample was recrystallized from dichloromethane to give colorless crystals containing solvent molecules in 1 : 1 molar ratio. Found: C, 83.48; H, 7.01%; MH^+ (FAB) 675. Calcd for $C_{52}H_{50}\cdot CH_2Cl_2$: C, 83.77; H, 6.90%; MH^+ 675. ^{1}H NMR ($CDCl_3$) δ = 2.20 (12H, s), 2.52 (6H, s), 2.57 (6H, s), 3.03 (4H, s), 5.65 (2H, s), 6.74 (4H, s), 7.03—7.15 (4H, dd, J = 6.8 and 2.0 Hz), 8.09 (4H, d, J = 7.3 Hz).

9-*t*-Butyl-4-methyl-1-[(2-pyridylthio)methyl]triptycene (10). Mp 226.0—227.5 °C. Found: C, 83.07; H, 6.72; N, 2.91%. Calcd for $C_{31}H_{29}NS$: C, 83.18; H, 6.53; N, 3.13%. ^{1}H NMR ($CDCl_3$) δ = 2.07 (3H, s), 2.31 (6H, s), 2.50 (3H, s), 4.89 (2H, s), 5.58 (1H, s), 6.81 (1H, d, J = 8.0 Hz), 6.95—7.02 (5H, m), 7.10 (1H, d, J = 8.0 Hz), 7.11 (1H, d, J = 8.1 Hz), 7.36 (2H, m), 7.45 (1H, dt, J = 7.8 and 1.7 Hz), 7.90 (2H, m), 8.49 (1H, m). This compound was also obtained by an independent route as follows. To a suspension of 22 mg (0.20 mmol) of 2-pyridinethiol and 6.4 mg (0.28 mmol) of sodium hydride in 3 mL of THF was added 50 mg (0.13 mmol) of the chloride **12** at room temperature. The whole was stirred overnight and quenched in a usual manner. The desired sulfide was obtained in 65% yield with recovery of the chloride in ca 20%.

1,2-Bis[9-(1,1-dimethylethyl)-4-methyl-1-triptycyl]ethane (11). Mp > 350 °C (decomp). Found: C, 92.18; H, 7.52%; M^+(EI) 674. Calcd for $C_{52}H_{50}$: C, 92.53; H, 7.47%; M 674. ^{1}H NMR ($CDCl_3$) δ = 1.94 (6H, s), 2.03 (12H, s), 2.51 (6H, s), 3.34 (4H, s), 5.58 (2H, s), 6.72 and 6.82 (4H, ABq, J = 8.0 Hz), 6.92—7.02 (8H, m), 7.36 (4H, m), 7.79 (4H, app. d, J = 7.0 Hz).

UV-vis Spectra. Spectra of *ap*-**4** and *sc*-**4** were measured on a Hitachi U-2000 spectrometer for chloroform solutions of ca. 8×10^{-5} mol dm^{-3}. Measurements at high concentration (ca. 5×10^{-3} mol dm^{-3}) gave no absorptions at > 450 nm for both the compounds, this meaning that ε_{max} of the absorptions in the region is less than 10, if present.

CINDO/S Calculation. Calculation was performed for 2(1*H*)-thioxo-1-pyridyl acetate on a convex computer with the CINDO/S program.[50] The input structure was optimized by the MOPAC93 program[51] at the PM3 level. The calculated transitions at > 250 nm are as follows with oscillater strength and the electronic transition in parentheses: 579.5 (0.0003 $n-\pi^*_{C=S}$), 344.6 (0.3807, $\pi-\pi^*_{C=S}$), 288.8 (0.0084, $n-\pi^*_{C=O}$), 285.1 (0.3201, $\pi-\pi^*_{C=S}$), 264.7 (0.0298, $n-\pi^*_{C=S}$).

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References

1) For Part 36 of the series, see M. Ōki, T. Miyasaka, Y. Taguchi, and S. Toyota, *Gazz. Chim. Ital.*, in press.

2) A preliminary communication has been published: S. Toyota and M. Ōki, *Tetrahedron Lett.*, **36**, 903 (1995)

3) M. Ōki, "The Chemistry of Rotational Isomers," Springer, Heidelberg (1993), Chap. 4.

4) M. Ōki, Y. Taguchi, T. Okamoto, T. Miyasaka, K. Hamada, S. Toyota, K. Yonemoto, and G. Yamamoto, *Bull. Chem. Soc. Jpn.*, **66**, 3790 (1993).

5) M. Ōki, Y. Taguchi, T. Miyasaka, M. Kitano, S. Toyota, T. Tanaka, K. Yonemoto, and G. Yamamoto, *Bull. Chem. Soc. Jpn.*, **68**, 1485 (1995).

6) R. A. Sheldon and J. K. Kochi, *Org. React.*, **19**, 279 (1972).

7) D. H. R. Barton, D. Crich, and W. B. Motherwell, *J. Chem. Soc., Chem. Commun.*, **1983**, 939.

8) D. H. R. Barton, D. Crich, and W. B. Motherwell, *Tetrahedron*, **41**, 3901 (1985).

9) D. Crich, *Aldrichimica Acta*, **20**, 35 (1987).

10) T. Tanaka, K. Yonemoto, Y. Nakai, G. Yamamoto, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **61**, 3239 (1988).

11) P. E. Eaton and Y.-C. Yip, *J. Am. Chem. Soc.*, **113**, 7692 (1991).

12) M. Newcomb and A. G. Glenn, *J. Am. Chem. Soc.*, **111**, 275 (1989).

13) S. Toyota, M. Endo, M. Teruhi, Y. Noda, M. Ōki, M. Yamasaki, and T. Shibahara, *Bull. Chem. Soc. Jpn.*, **66**, 2088 (1993).

14) M. Ōki, Y. Taguchi, and S. Toyota, *Bull. Chem. Soc. Jpn.*, **65**, 2616 (1992).

15) D. H. R. Barton, D. Bridon, I. Fernandez-Picot, and S. Z. Zard, *Tetrahedron*, **43**, 2733 (1987).

16) Although the authors in Ref. 15 postulated that the photodecomposition of the ester would be slow at low temperatures, it does not lead to accumulation of the radicals, as they anticipated. Rather it should be assumed that the addition of the radical to the thioxo moiety becomes slow at low temperatures because of the presence of activation energy and/or the cage effect. The reason for the difference between the present work and that of Ref. 15 may well be the difference in concentrations. Whereas Barton et al. prefer ca. 0.1 mol dm^{-3} solutions, the concentrations used in this work are lower than that by one order of magnitude. The lower concentration could make the cage effect more significant than the case of the higher concentration.

17) D. H. R. Barton, P. Blundell, and J. Cs. Jaszberenyi, *J. Am. Chem. Soc.*, **113**, 6937 (1991).

18) J. W. Wilt, "Free Radical Rearrangement," in "Free Radicals," ed by J. K. Kochi, Vol. I, John Wiley, New York (1973), Chap. 8.

19) W. H. Urry and M. S. Kharasch, *J. Am. Chem. Soc.*, **66**, 1438 (1994).

20) F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **76**, 3732 (1954).

21) C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiaonnou, *J. Am. Chem. Soc.*, **92**, 4927 (1970).

22) A. Rembaum and M. Szwarc, *J. Chem. Phys.*, **23**, 909 (1955).

23) J. Smid, A. Rembaum, and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 3315 (1956).

24) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1389 (1968).

25) A. T. Bomquist and A. F. Ferris, *J. Am. Chem. Soc.*, **73**, 3408

(1951).
26) C. Walling and E. S. Savas, *J. Am. Chem. Soc.*, **82**, 1738 (1960).
27) D. F. de Tar, R. A. J. Long, J. Rendleman, J. Bradley, and P. Duncan, *J. Am. Chem. Soc.*, **89**, 4051 (1967).
28) M. Mikami, K. Toriumi, M. Konno, and Y. Saito, *Acta Crystallogr., Sect. B*, **31**, 2474 (1975).
29) R. Isaksson, M. Ōki, J. Sandström, M. R. Suissa, and S. Toyota, *Acta Chem. Scand.*, **47**, 570 (1993).
30) S. Toyota, T. Miyasaka, Y. Matsumoto, T. Matsuo, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **67**, 1680 (1994).
31) G. Bott, L. D. Field, and S. Sternhell, *J. Am. Chem. Soc.*, **102**, 5618 (1980).
32) T. J. Burkey, D. Griller, L. Lunazzi, and A. S. Nazran, *J. Org. Chem.*, **48**, 3704 (1983).
33) F. G. Edward and F. R. Mayo, *J. Am. Chem. Soc.*, **72**, 1265 (1950).
34) J. D. Bradley and A. P. Roth, *Tetrahedron Lett.*, **1971**, 3907.
35) T. Nakata, K. Tokumaru, and O. Simamura, *Tetrahedron Lett.*, **1967**, 3303.
36) T. Koenig, M. Deinzner, and J. A. Hoobler, *J. Am. Chem. Soc.*, **93**, 938 (1971).
37) T. Koenig and J. A. Hoobler, *Tetrahedron Lett.*, **1972**, 1803.
38) E. G. Bagryanskaya, Yu. A. Grishin, R. Z. Sagdeev, and Yu. N. Molin, *Chem. Phys. Lett.*, **114**, 138 (1985).
39) W. F. Smith and B. W. Rossiter, *Tetrahedron*, **25**, 2059 (1969).
40) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 3413 (1965).
41) J. D. Coyle, *Tetrahedron*, **41**, 5393 (1983).
42) P. de Mayo and R. Suau, *J. Am. Chem. Soc.*, **96**, 6807 (1974).
43) A. Couture, K. Ho, M. Hoshino, P. de Mayo, R. Suau, and W. R. Ware, *J. Am. Chem. Soc.*, **98**, 6218 (1976).
44) K. W. Ho and P. de Mayo, *J. Am. Chem. Soc.*, **101**, 5725 (1979).
45) S. Basu, A. Couture, K. W. Ho, M. Hoshino, P. de Mayo, and R. Suau, *Can. J. Chem.*, **59**, 246 (1981).
46) A modified version of QCPE program (#0382) by S. Kishimoto of Osaka City University.
47) C. Bohne, R. Boch, and J. C. Scaiano, *J. Org. Chem.*, **55**, 5414 (1990).
48) A referee suggested that the UV-D36C filter will allow passage of the light of 313 nm wavelength. However, because of the weak nature of the transmitting light, we believe the conclusion stated here would not have to be changed.
49) D. Griller, P. R. Marriott, D. C. Nonhebel, M. J. Perkins, and P. C. Wong, *J. Am. Chem. Soc.*, **103**, 1981 (1981).
50) R. C. Parish and L. M. Stock, *J. Org. Chem.*, **31**, 4265 (1966).
51) MOPAC93 of Fijitsu Limited, Tokyo, programed by J. J. P. Stewart.