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Reactivities of Stable Rotamers. XXXIX. Thermal Decomposition of *t*-Butyl 3-Methyl-3-(substituted 9-triptycyl)peroxybutanoate Rotamers[1)]

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The *ap* and *sc* rotamers of the title compound, where substituents are 1,4-dimethyl, 1,4-dimethoxy, 1,2,3,4-tetrafluoro, and 1,2,3,4-tetrachloro, were thermolyzed in toluene solutions to examine the effects of interactions between the radical center and the substituent. The rates of thermolyses were affected neither by the substituent nor by the rotameric positions, but the product distributions showed dependence on the substituent. In the *ap*-forms, the effectively bulkier the substituent at the 1-position, the higher the yields of the 5-membered ring compound. This was attributed to the degree of the tilting of the 9-substituent, which forces the radical center to be pushed into the triptycene skeleton. For the *sc*-forms, the chloro and the methyl substituents exhibited special effects, the former affording a colligation product between benzyl and 2-(1,2,3,4-tetrachloro-9-triptycyl)-2-methylpropyl radicals and the latter showing a tendency of radical migration to the benzylic position. Comparison of the results of thermolyses of the 1,4-dimethyl peroxyester with those of 2(1*H*)-thioxo-1-pyridyl 3-(1,4-dimethyl-9-triptycyl)-3-methylbutanoate indicates that, although it is believed that these precursors afford the same 2-(1,4-dimethyl-9-triptycyl)-2-methylpropyl radicals, the product distributions were significantly different from each other. These results were attributed to the stabilizing effects of the sulfur compound on the radical in the solvent cage in the latter.

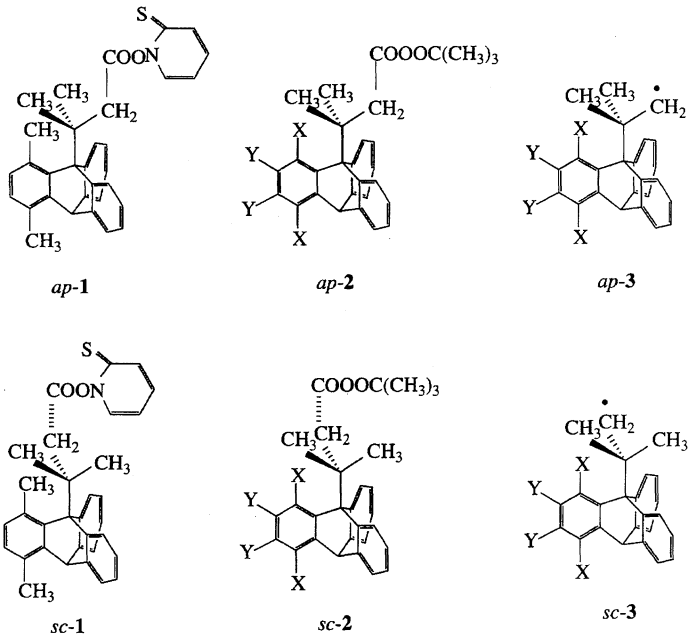
Thermolyses and photolyses of *ap*- and *sc*-rotamers of 2(1*H*)-thioxo-1-pyridyl 3-(1,4-dimethyl-9-triptycyl)-3-methylbutanoate (**1**) have shown interesting differences in product distributions as well as in dependence on the phase.[2)] Classical typical radical reactions are thermolyses of *t*-butyl peroxycarboxylate[3)] and, if we use *t*-butyl *ap*- and *sc*-3-(1,4-dimethyl-9-triptycyl)-3-methylperoxybutanoate (**2**: X=CH_3, Y = H), the intermediate radicals should be identical with those produced from **1**, although their environments including solvent cages should be different. Therefore it is an interesting question to ask ourselves whether the 2-(1,4-dimethyl-9-triptycyl)-2-methylpropyl radicals (**3**: X = CH_3, Y = H) produced by the two methods behave similarly or differently (Scheme 1).

In addition to these interesting questions, stability of the intervening radicals may be affected by the substituents if they are in close proximity to the radical center. In this respect, the *ap*- and the *sc*-forms should behave quite differently, as was observed in the decomposition of compound **1**. We therefore decided to carry out studies on thermal decomposition of variously substituted *t*-butyl 3-methyl-3-(9-triptycyl)peroxybutanoate (**2**) rotamers to see the substituent effects both on rates of decomposition and product distributions as well as the differences due to rotational isomerism.

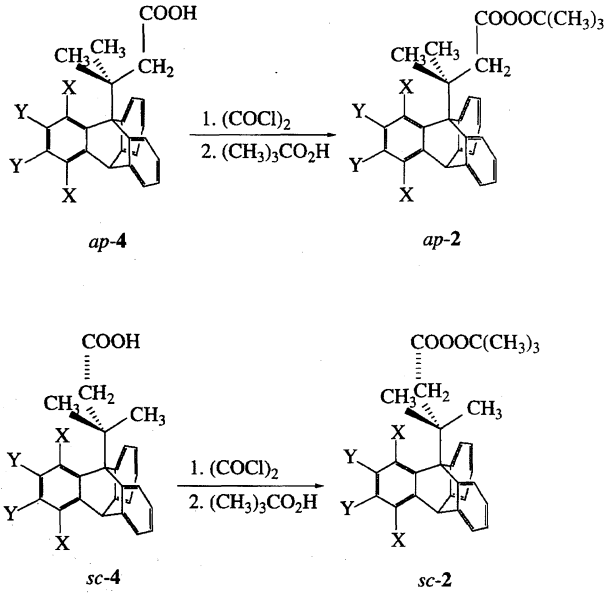
Preparation of the *t*-butyl peroxyesters **2** were straightforward, because most of the corresponding carboxylic acids **4** were known (Scheme 2). These carboxylic acids were converted to acid chlorides and then treated with *t*-butyl hydroperoxide in the presence of pyridine. These peroxyesters were dissolved in toluene and heated in sealed tubes at 120 °C to effect decomposition.

X-Ray Structures. In order to discuss the reactivity of the compounds, it is important to know the structure of the original system. Since the *t*-alkyl substituent at the 9-position of the triptycene skeleton is known to be bent away from the 1-substituent to release steric strain[4—6)] and this effect of the 1-substituent is expected to be larger when the substituent becomes large, we carried out the determination of structures of the *t*-butyl esters (**2**) by X-ray analysis. Unfortunately the tetrafluoro compound failed to give suitable crystals for X-ray diffraction in spite of various efforts, but others gave satisfactory results for comparison.

The results are shown as ORTEP drawings (Fig. 1) and in Tables 1, 2, 3, and 4. Bond angles inside of the carbon 9 are smaller than the tetrahedral value to accommodate the strained structure of triptycene. To compensate these angles,



Scheme 1.



Scheme 2.

outside angles of the triptycene skeleton at carbon 9 are all larger than the normal value. When one examines the effect of the bulkiness of the 1-substituent, one notices the tendency that the larger the bulk of the 1-substituent, the larger the sum of the bond angle C(9a)–C(9)–C(17) and that of A–C(1)–C-(9a) (Table 5).

Even though the methoxy group is small with respect to the methyl, it has a tendency to resist to bending in the plane[7–9] and the tendency is reproduced here. The data, C(9a)–C-(9)–C(17) angles, suggest that the 1-chloro substituent more severely distorts the structure than the 1-methyl substituent. Although this is contrary to the expectation from the van der Waals radii of a methyl and a chloro group,[10] we must also take into account the buttressing effect for the 1,2,3,4-tetrachloro compound. Indeed, the bond angle of C(9a)–C(1)–C-(26) is large (130° in the methyl compound) with respect to that of C(9a)–C(1)–Cl(1), which is 125° in the chloro compound. Thus the 1-chloro substituent pushes away the 9-*t*-alkyl group more effectively than the 1-methyl group with the help of the buttressing effects.

The angles C(8a)–C(9)–C(17) and C(9)–C(17)–C(18) are almost the same irrespective of the kinds of the 1-substituent. The C(9a)–C(9)–C(17) angles are not much different from each other when there is a 1-substituent. As a consequence the 9-substituent, the methylene group attached to the peroxyester moiety in particular, is pushed into the triptycene skeleton. This pushing is not seen clearly from the non-bonding distance between the CH_2 group attached to the peroxyester moiety and the benzene rings which flank the group, as is seen in Table 6. Rather, the pushing is correlated with the dihedral angles made by the benzeno bridges (Table 7). The order of the effective sizes of the substituents is Cl > CH_3 > OCH_3 > H. Although the X-ray structure of the fluoro compound is not known, the effective size of the fluoro substituent can be placed between that of the methoxy group and that of the hydrogen.

The structure has significance in two ways: One is that the radical produced at this site will effectively interact with the benzeno bridges which flank the radical center as it is pushed into the triptycene skeleton and the second is that the radical could be protected against the external attack due to the steric effects of the triptycene skeleton.

Rates of Decomposition. The rates of decomposition of compound **2** are summarized in Table 8, which reveals that the rates are surprisingly constant: They neither depend on rotational isomerism, nor on the substituents.

Steric effects by the 1-substituent, especially for the *sc*-forms, could be significant if the steric congestion, for example, is released in the transition state of the reaction. The tran-

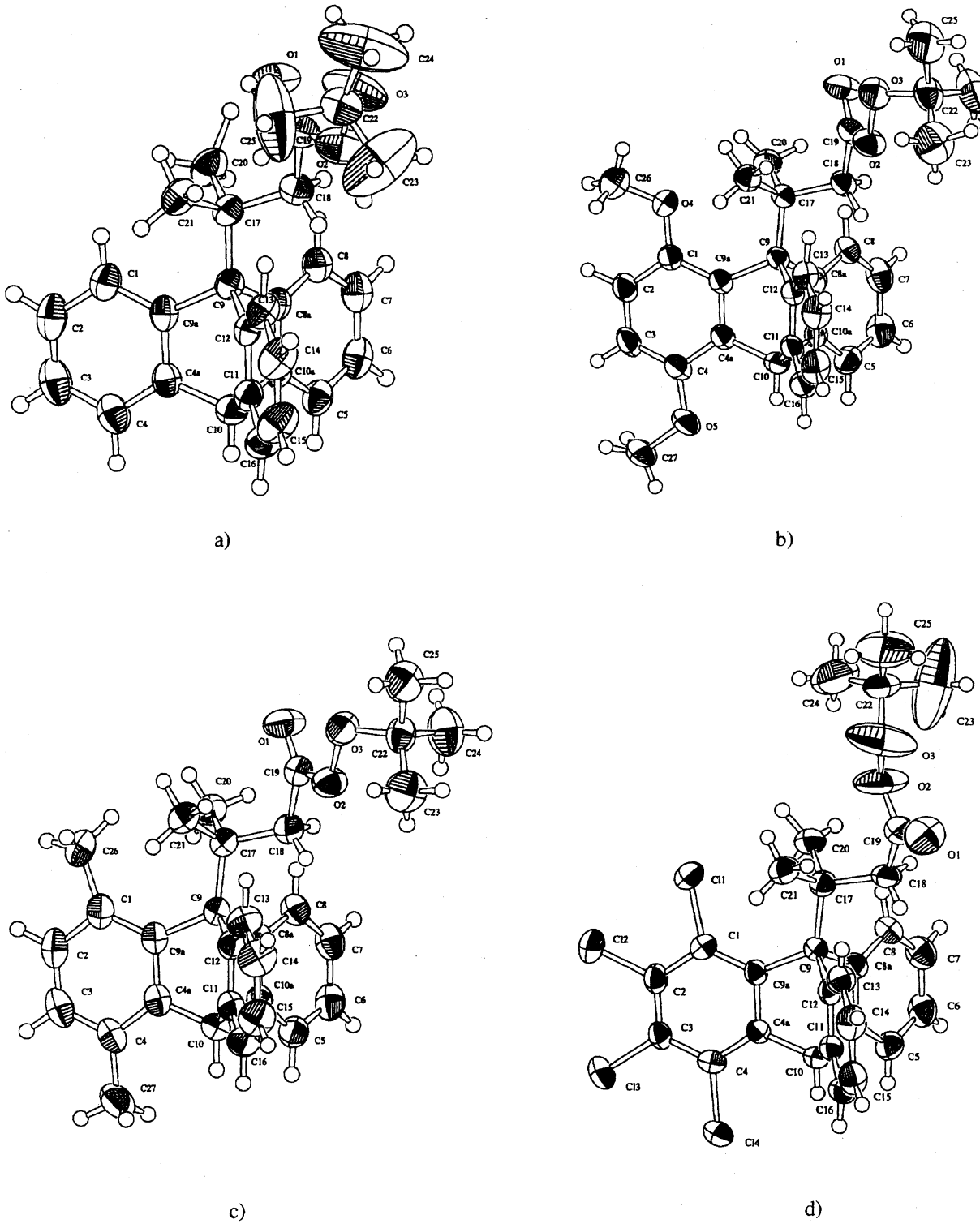


Fig. 1. ORTEP drawings of *t*-butyl *ap*-3-methyl-3-(substituted 9-triptycyl)peroxybutanoate (**2**) with thermal elipsoids at 50% probability: a) unsubsititued, b) 1,4-dimethoxy, c) 1,4-dimethyl, and d) 1,2,3,4-tetrachloro.

sition structures of the rate-limiting step in the decomposition of peroxyesters are somewhat controversial in thermolyses,[11] whereas the O–O bond scission is clearly the rate-limiting step in photolyses.[12] The present data indicate that the rate-limiting step in these thermolyses must be the O–O bond scission. Because the O–O bond is located far from the substituent even in the *sc* form and the bond-lengthening in the transition state would not affect the steric situation between the methylene group alpha to the carbonyl group and the 1-substituent, the substituent and the rotational positions have nothing to do with the transition structure.

Participation of a substituent in the homolysis of *o*-substi-

Table 1. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in *t*-Butyl 3-Methyl-3-(9-triptycyl)peroxybutanoate[a)]

Atom	*x*	*y*	*z*	B_{eq}[b)]
O(1)	0.1843(3)	0.4081(2)	0.0818(3)	6.99(9)
O(2)	0.1109(3)	0.4518(2)	0.2950(3)	6.14(8)
O(3)	0.1080(4)	0.3470(2)	0.2953(3)	8.58(10)
C(1)	0.4697(4)	0.7337(3)	0.1112(4)	4.20(10)
C(2)	0.5658(4)	0.7879(4)	0.1032(5)	5.5(1)
C(3)	0.5560(5)	0.8820(4)	0.1694(5)	5.9(1)
C(4)	0.4490(4)	0.9250(3)	0.2464(4)	4.6(1)
C(4a)	0.3523(3)	0.8721(2)	0.2539(3)	3.47(8)
C(5)	−0.0275(4)	0.9913(3)	0.1862(4)	3.92(9)
C(6)	−0.1476(4)	0.9810(3)	0.0800(4)	4.24(10)
C(7)	−0.1455(4)	0.8876(3)	0.0116(4)	4.12(10)
C(8)	−0.0249(4)	0.8033(3)	0.0472(4)	3.61(9)
C(8a)	0.0957(3)	0.8120(2)	0.1543(3)	3.04(8)
C(9)	0.2420(3)	0.7283(2)	0.2108(3)	3.01(7)
C(9a)	0.3604(3)	0.7755(2)	0.1874(3)	3.31(8)
C(10)	0.2309(4)	0.9115(3)	0.3331(4)	3.60(9)
C(10a)	0.0924(3)	0.9080(2)	0.2217(3)	3.24(8)
C(11)	0.2559(3)	0.8329(2)	0.4429(3)	3.35(8)
C(12)	0.2618(3)	0.7356(2)	0.3815(3)	3.11(8)
C(13)	0.2837(4)	0.6580(3)	0.4748(4)	3.90(9)
C(14)	0.3000(4)	0.6789(3)	0.6253(4)	5.0(1)
C(15)	0.2945(4)	0.7749(3)	0.6832(4)	5.3(1)
C(16)	0.2725(4)	0.8534(3)	0.5923(4)	4.5(1)
C(17)	0.2502(3)	0.6184(2)	0.1416(3)	3.51(8)
C(18)	0.1234(4)	0.5849(3)	0.1717(5)	3.98(10)
C(19)	0.1482(4)	0.4714(3)	0.1729(4)	4.8(1)
C(20)	0.2321(6)	0.6131(4)	−0.0269(4)	4.9(1)
C(21)	0.3996(5)	0.5422(3)	0.2077(5)	4.4(1)
C(22)	0.1966(4)	0.3053(3)	0.4325(4)	4.9(1)
C(23)	0.1440(8)	0.3656(4)	0.5556(7)	13.9(2)
C(24)	0.1747(8)	0.2020(4)	0.4223(6)	14.2(2)
C(25)	0.3454(6)	0.2996(5)	0.4438(8)	14.4(3)

a) Values in parentheses are estimated standard deviations.
b) $B_{eq}/\text{Å}^2 = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in *t*-Butyl 3-(1,4-Dimethoxy-9-triptycyl)-3-methylperoxybutanoate[a)]

Atom	*x*	*y*	*z*	B_{eq}[b)]
O(1)	0.2963(2)	0.9807(1)	0.5040(2)	5.58(6)
O(2)	0.3068(2)	0.9476(1)	0.7343(2)	4.71(5)
O(3)	0.1602(2)	1.0038(1)	0.7035(2)	5.39(5)
O(4)	0.4576(2)	0.6392(1)	0.3033(2)	4.04(4)
O(5)	0.9535(2)	0.4357(1)	0.6692(2)	4.79(5)
C(1)	0.5807(3)	0.5885(2)	0.3949(3)	3.20(6)
C(2)	0.6272(3)	0.5015(2)	0.3435(3)	3.99(7)
C(3)	0.7519(3)	0.4493(2)	0.4294(3)	4.16(7)
C(4)	0.8314(3)	0.4825(2)	0.5708(3)	3.57(6)
C(4a)	0.7849(3)	0.5694(2)	0.6226(3)	3.12(6)
C(5)	1.0471(3)	0.7088(2)	0.8100(3)	4.12(7)
C(6)	1.0761(3)	0.7845(2)	0.7749(4)	4.85(8)
C(7)	0.9626(3)	0.8411(2)	0.6846(4)	4.49(8)
C(8)	0.8206(3)	0.8250(2)	0.6328(3)	3.50(6)
C(8a)	0.7879(3)	0.7505(2)	0.6706(3)	2.91(5)
C(9)	0.6353(3)	0.7207(1)	0.6251(3)	2.80(5)
C(9a)	0.6604(3)	0.6252(1)	0.5373(3)	2.84(5)
C(10)	0.8625(3)	0.6091(2)	0.7801(3)	3.44(6)
C(10a)	0.9060(3)	0.6915(2)	0.7576(3)	3.06(5)
C(11)	0.7475(3)	0.6387(2)	0.8575(3)	3.26(6)
C(12)	0.6255(3)	0.6975(2)	0.7775(3)	2.98(5)
C(13)	0.5122(3)	0.7268(2)	0.8396(3)	3.64(6)
C(14)	0.5219(4)	0.6975(2)	0.9760(3)	4.59(8)
C(15)	0.6434(4)	0.6395(2)	1.0524(3)	4.81(8)
C(16)	0.7567(4)	0.6099(2)	0.9930(3)	4.06(7)
C(17)	0.5014(3)	0.7923(2)	0.5421(3)	3.06(5)
C(18)	0.5042(3)	0.8802(2)	0.6510(3)	3.43(6)
C(19)	0.3584(3)	0.9426(2)	0.6151(3)	3.75(6)
C(20)	0.5123(4)	0.8135(2)	0.3906(3)	3.97(7)
C(21)	0.3533(3)	0.7617(2)	0.5080(4)	3.72(7)
C(22)	0.1631(3)	1.0675(2)	0.8355(4)	5.26(8)
C(23)	0.1990(7)	1.0178(4)	0.9748(6)	8.0(1)
C(24)	0.2679(6)	1.1285(3)	0.8544(8)	7.8(1)
C(25)	0.0039(5)	1.1153(4)	0.7846(8)	8.3(1)
C(26)	0.3467(4)	0.5957(3)	0.1975(4)	5.30(9)
C(27)	1.0086(5)	0.3486(2)	0.6144(5)	5.79(9)

a) Values in parentheses are estimated standard deviations.
b) $B_{eq}/\text{Å}^2 = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

tuted peroxybenzoates is reported.[13)] The effect is very large when the substituent is sulfur and is significant when the substituent is a large halogen. It is reasonable that we do not observe the substituent effects on the homolysis in the present work. In the peroxybenzoate decomposition, the radicals are stabilized by the substituent by forming a five-membered ring with the carboxyl radical, whereas in our case the radical center and the 1-substituent would have to be members of an 8-membered ring, which is not preferred due to the entropy effects, if the anchimeric assistance were to take place. In addition, such a conformation is of prohibitively high energy due to the steric effect of the triptycene system. We therefore believe that the absence of the substituent effects on the rates of decomposition is due to the fact that the O–O bond scission, which is the rate-limiting step, takes place at a site distant from the substituent.

Product Distributions. The results of the product analysis are shown in Tables 9 and 10, for *ap*- and *sc*-isomers, respectively.

First of all, the results obtained for the rotational isomers will be compared. In order to discuss the effect of the 1-substituent, it is necessary to know the results of the unsubstituted peroxyester. The results of the unsubstituted compounds show that the main product from this is 9-*t*-butyltriptycene (**6**: X = Y = H) together with a smaller amount of 9-(2-*t*-butoxy-1,1-dimethylethyl)triptycene (**5**: X = Y = H). In addition, there was obtained 15% 9-(3-phenyl-1,1-dimethylpropyl)triptycene (**8**: X = Y = H) which is apparently the colligation product from the radical **3** (X = Y = H) and benzyl radical which is produced by abstraction of hydrogen from toluene. Such results indicate that the radical **3** (X = Y = H) tends to abstract hydrogen from the solvent toluene but radical recombination in the solvent cage[14)] is also important. Since the molecule has a local C_{3v} symmetry if we replace the peroxyester moiety by a hydrogen, the *t*-alkyl moiety is not bent and the results can be taken as typical when steric

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in *t*-Butyl 3-(1,4-Dimethyl-9-triptycyl)-3-methylperoxybutanoate[a)]

Atom	*x*	*y*	*z*	B_{eq}[b)]
O(1)	0.6489(2)	0.2378(1)	0.1638(2)	6.17(4)
O(2)	0.6479(2)	0.35287(9)	0.0292(2)	5.18(4)
O(3)	0.7905(2)	0.37135(9)	0.1402(2)	5.33(4)
C(1)	0.2808(2)	0.0105(1)	−0.4395(3)	4.24(5)
C(2)	0.2010(3)	−0.0493(1)	−0.5635(3)	5.03(6)
C(3)	0.0912(3)	−0.0272(2)	−0.6890(3)	5.11(6)
C(4)	0.0544(2)	0.0591(1)	−0.7023(2)	4.35(5)
C(4a)	0.1304(2)	0.1199(1)	−0.5791(2)	3.78(4)
C(5)	−0.0824(2)	0.2786(1)	−0.4225(3)	4.24(5)
C(6)	−0.1141(2)	0.2973(1)	−0.2731(3)	4.68(5)
C(7)	−0.0155(2)	0.2782(1)	−0.1339(3)	4.46(5)
C(8)	0.1173(2)	0.2426(1)	−0.1390(3)	3.83(5)
C(8a)	0.1538(2)	0.2252(1)	−0.2867(2)	3.33(4)
C(9)	0.2969(2)	0.1845(1)	−0.3201(2)	3.30(4)
C(9a)	0.2412(2)	0.0988(1)	−0.4439(2)	3.58(4)
C(10)	0.0937(2)	0.2153(1)	−0.5817(2)	3.87(5)
C(10a)	0.0504(2)	0.2430(1)	−0.4262(2)	3.51(4)
C(11)	0.2305(2)	0.2618(1)	−0.5674(2)	3.69(4)
C(12)	0.3398(2)	0.2464(1)	−0.4307(2)	3.48(4)
C(13)	0.4698(2)	0.2873(1)	−0.4093(3)	4.48(5)
C(14)	0.4879(3)	0.3416(2)	−0.5193(3)	5.47(6)
C(15)	0.3791(3)	0.3563(2)	−0.6520(3)	5.38(6)
C(16)	0.2494(3)	0.3162(1)	−0.6767(3)	4.56(5)
C(17)	0.4187(2)	0.1762(1)	−0.1580(2)	3.66(4)
C(18)	0.4463(2)	0.2686(1)	−0.0590(3)	4.08(5)
C(19)	0.5917(2)	0.2804(1)	0.0595(2)	3.92(5)
C(20)	0.3729(3)	0.1165(2)	−0.0475(3)	4.62(6)
C(21)	0.5608(2)	0.1417(2)	−0.1973(3)	4.54(5)
C(22)	0.8003(2)	0.4650(1)	0.1787(3)	4.47(5)
C(23)	0.7665(5)	0.5079(2)	0.0241(4)	7.03(9)
C(24)	0.7037(4)	0.4965(3)	0.2855(5)	7.4(1)
C(25)	0.9562(3)	0.4744(2)	0.2699(5)	6.75(8)
C(26)	0.4018(4)	−0.0325(2)	−0.3238(4)	6.05(7)
C(27)	−0.0653(3)	0.0839(2)	−0.8420(3)	6.01(7)

a) Values in parentheses are estimated standard deviations.
b) $B_{eq}/Å^2 = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 4. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in *t*-Butyl 3-Methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)peroxybutanoate[a)]

Atom	*x*	*y*	*z*	B_{eq}[b)]
Cl(1)	0.71305(10)	0.23028(9)	0.7540(1)	5.74(5)
Cl(2)	0.8215(1)	0.2000(1)	0.8870(1)	6.39(5)
Cl(3)	0.90132(8)	0.0555(1)	0.8868(1)	4.88(4)
Cl(4)	0.87036(7)	−0.06671(9)	0.7414(1)	4.08(4)
O(1)	0.5750(3)	0.2076(3)	0.3506(4)	6.7(2)
O(2)	0.5353(4)	0.2490(4)	0.4808(4)	10.1(2)
O(3)	0.5269(4)	0.3218(4)	0.4212(5)	11.9(3)
C(1)	0.7528(3)	0.1456(3)	0.7412(4)	3.3(1)
C(2)	0.8037(3)	0.1338(4)	0.8061(4)	3.6(1)
C(3)	0.8394(3)	0.0688(3)	0.8066(4)	3.1(1)
C(4)	0.8252(3)	0.0153(3)	0.7419(4)	3.1(1)
C(4a)	0.7751(3)	0.0258(3)	0.6791(4)	2.7(1)
C(5)	0.6564(4)	−0.1154(4)	0.6366(5)	4.1(2)
C(6)	0.5894(4)	−0.1218(4)	0.6519(5)	4.4(2)
C(7)	0.5505(4)	−0.0596(4)	0.6506(5)	4.4(2)
C(8)	0.5769(3)	0.0095(4)	0.6303(4)	3.6(1)
C(8a)	0.6449(3)	0.0179(3)	0.6138(4)	2.9(1)
C(9)	0.6850(3)	0.0904(3)	0.5921(4)	2.8(1)
C(9a)	0.7374(3)	0.0927(3)	0.6751(4)	2.7(1)
C(10)	0.7566(3)	−0.0314(3)	0.6075(4)	3.1(1)
C(10a)	0.6838(3)	−0.0461(3)	0.6190(4)	3.0(1)
C(11)	0.7668(3)	0.0062(3)	0.5173(4)	3.0(1)
C(12)	0.7308(3)	0.0718(3)	0.5081(4)	2.9(1)
C(13)	0.7404(3)	0.1115(4)	0.4282(5)	3.7(2)
C(14)	0.7849(4)	0.0882(4)	0.3610(5)	4.3(2)
C(15)	0.8191(3)	0.0231(4)	0.3714(5)	4.4(2)
C(16)	0.8106(3)	−0.0180(4)	0.4505(4)	3.7(2)
C(17)	0.6376(3)	0.1600(3)	0.5737(4)	3.3(1)
C(18)	0.5934(4)	0.1385(4)	0.4895(5)	3.8(2)
C(19)	0.5690(4)	0.2017(4)	0.4305(5)	4.5(2)
C(20)	0.5910(4)	0.1777(5)	0.6559(5)	4.3(2)
C(21)	0.6802(4)	0.2302(4)	0.5492(6)	4.3(2)
C(22)	0.4712(4)	0.3561(4)	0.4646(6)	5.8(2)
C(23)	0.4188(10)	0.3083(9)	0.4494(10)	18.9(7)
C(24)	0.4804(8)	0.3703(7)	0.5606(9)	13.2(5)
C(25)	0.4649(8)	0.4222(6)	0.402(1)	14.2(5)

a) Values in parentheses are estimated standard deviations.
b) $B_{eq}/Å^2 = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 5. Selected Bond Angles (°) in *t*-Butyl Peroxyesters (*ap*-**2**)

Atoms X–Y–Z	H	1,4-$(CH_3O)_2$	1,4-$(CH_3)_2$	1,2,3,4-Cl_4
A–C(1)–C(9a)[a)]	—	120.0(2)	130.6(2)	125.1(5)
C(8a)–C(9)–C(17)	115.6(3)	113.4(2)	112.7(2)	112.2(4)
C(9a)–C(9)–C(17)	115.3(3)	118.0(2)	119.4(2)	119.9(5)
C(9)–C(17)–C(18)	108.4(3)	107.6(2)	108.1(1)	106.1(5)

a) A is the first atom of the 1-substituent.

effects are absent.

The plausible reaction paths for all the products from *ap*- and *sc*-**2** are summarized in Schemes 3 and 4, respectively, except for the *sc*-methyl compound *sc*-**2** (X = CH_3, Y = H).

When a fluoro substituent is introduced at the 1-position,[15] dramatic changes in the product distribution from the unsubstituted peroxyester are observed: The five-membered ring compound **7** (X=Y=F) was obtained from both *ap* and *sc* isomers at the expense of the colligation product **8** (X = Y = F). These results were common in all the 1-substituted compounds except for *sc*-**2** (X = CH_3, Y = H).

When the yields of **6** and **7** from *ap*- and *sc*-**2** (X = Y = F) are compared, one notices that, while *ap* gives more **7** but less **6** than the *sc* form, the differences are small. The yields of **5** are higher for *ap* than *sc*. We attribute these results to the structural features of the compounds concerned. We may assume that the intermediate radicals (**3**) take similar structures, as are shown by the X-ray structures of **2**, although the sp^2 hybridized structure of the radical should reduce steric interactions to some extent. Then the radical center in *ap*-**3** is pushed into the triptycene skeleton. This should cause, as was suggested in the discussion of the structure, steric protection against the external attack and the yield of **6** (X = Y = F) is decreased, whereas that of **7** increases because the distance between the unsubstituted benzeno bridge and the

Table 6. Selected Nonbonding Distances (Å) in *t*-Butyl Peroxyesters (*ap*-**2**)

Atoms X–Y	H	1,4-$(CH_3O)_2$	1,4-$(CH_3)_2$	1,2,3,4-Cl_4
C(18)–C(8)	3.136(5)	3.100(4)	3.103(3)	3.12(1)
C(18)–C(13)	3.121(6)	3.154(4)	3.118(3)	3.13(1)
C(20)–C(1)	3.202(6)	3.405(4)	3.449(3)	3.54(1)
C(20)–C(8)	3.208(6)	3.123(4)	3.087(3)	3.06(1)
C(21)–C(1)	3.188(6)	3.378(4)	3.486(3)	3.51(1)
C(21)–C(13)	3.110(6)	3.035(4)	3.033(3)	3.02(1)

Table 7. Dihedral Angles (°) Made by Benzeno Bridges in *t*-Butyl Peroxyesters (*ap*-**2**)

Planes A–B[a)]	H	1,4-$(CH_3O)_2$	1,4-$(CH_3)_2$	1,2,3,4-Cl_4
1–2	118.82	119.26	113.92	116.81
1–3	119.62	115.81	122.83	114.86
2–3	121.55	124.66	123.07	128.34

a) Plane 1 is made by C(1)–C(4), C(4a), and C(9a), plane 2 by C(5)–C(8), C(8a), and C(10a), and plane 3 by C(11)–C(16).

radical center is well within the bond-forming one. In the *sc*-isomer, by bending of the *t*-alkyl substituent away from the 1-substituent, the radical center is, relatively speaking, pushed out from the triptycene skeleton. If we take the averages of two *peri*-carbon–methyl distances shown in Table 6,[16] we notice that these distances are clearly larger than those of *peri*-carbon–C(18). This effect on the product distribution is seen as the decrease in the yield of **7** and as the increase in that of **6**.

When the 1-substituent becomes large, the bulkiness effects of the substituent become more outstanding than the fluorine case. For the *ap* compounds, the effectively bulkier the 1-substituent, the more abundant of the 5-membered ring **7** in the *ap* than in the *sc*. In contrast, the sum of the yields of the *t*-butoxy compound **5** and the *t*-butyl compound **6** decreases in the *sc* form, as the effective bulk of the 1-substituent increases, as is seen in the tetrachloro compound.

The case of *sc*-**2** (X = Y = Cl) was especially interesting because as much as 21% of the colligation product between the radical **3** (X = Y = Cl) and benzyl was obtained. This must be attributed to the stabilization of the radical by the chloro substituent which is close to the radical center. This type of radical stabilization by the chloro substituent has been noticed.[17,18] The rates of decomposition of acyloxyl radicals are known to be very large 10^9—10^{10} s^{-1},[19—23] an exceptional case being even larger 10^{11}—10^{12} s^{-1}[24] in the photolysis. Therefore, the results suggest that the chloro group, although it does not participate in the rate-limiting step of the peroxyester, does so in the stabilization of the intervening radical.

sc-**2** (X=CH_3, Y=H) showed interesting trends. The plausible mechanisms are shown in Scheme 5. The originally produced radical *sc*-**3** (X=CH_3, Y=H) rearranges very easily to the benzylic radical **11**, as was reported previously.[2,6] However, the feature of the present reaction is that it does afford the *t*-butoxy compound **5** before rearrangement, whereas in the Hunsdiecker chlorodecarboxylation no such product was detected.[6] The results indicate that the radical *sc*-**3** (X=CH_3, Y = H) has some lifetime, as was found in the thermolysis and photolysis of *sc*-**1**. The results together with those of *sc*-**1** suggest that the radical rearrangement from *sc*-**3**(X=CH_3,

Table 8. Rates of Decomposition of *t*-Butyl Peroxyesters (**2**) (10^{-4} s^{-1}) in Toluene at 120 °C

Substituents	H	1,2,3,4-F_4	1,4-$(CH_3O)_2$	1,4-$(CH_3)_2$	1,2,3,4-Cl_4
ap	1.3±0.1	1.5±0.1	3.1±0.2	2.4±0.2	2.4±0.2
sc	1.3±0.1	1.5±0.1	2.4±0.2	1.8±0.2	2.6±0.2

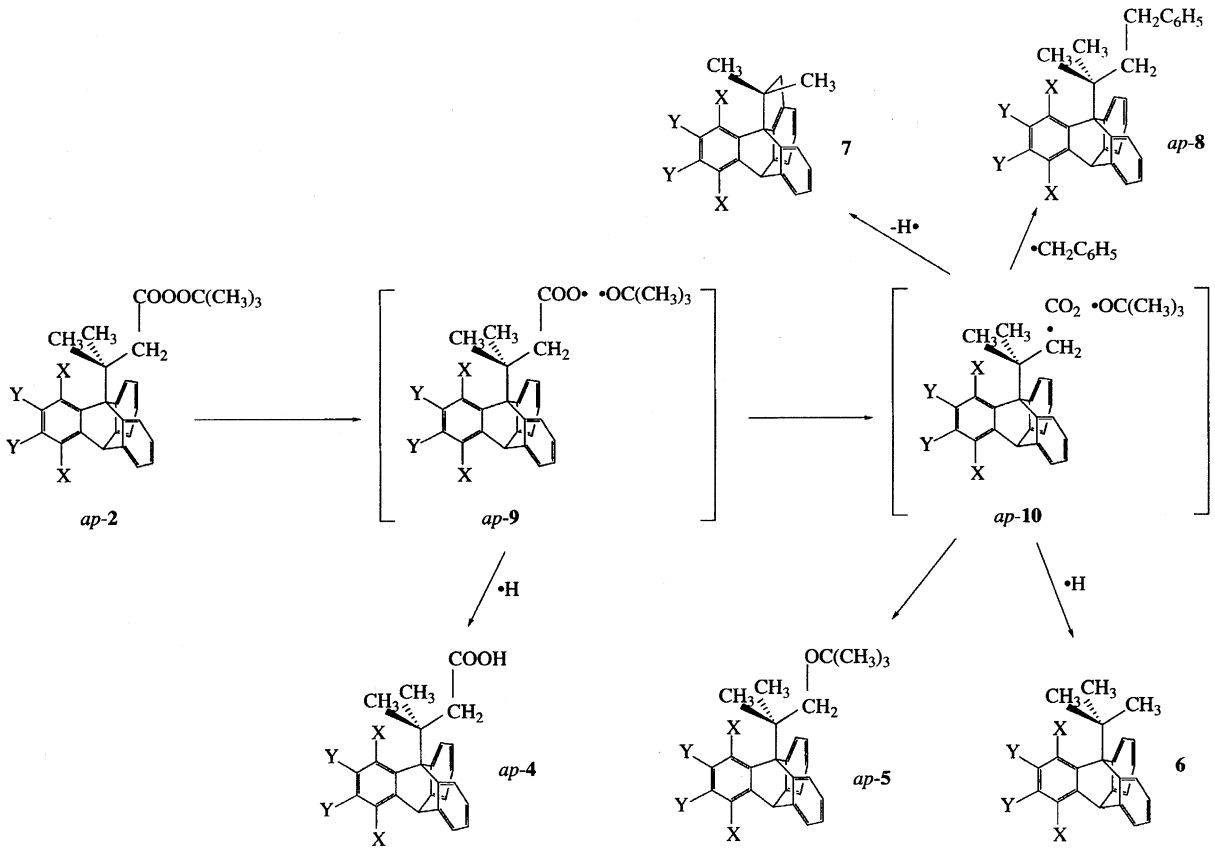
Table 9. Product Distributions (%) in Thermolyses of *t*-Butyl *ap*-Peroxyesters (*ap*-**2**)

Substituents	H	1,2,3,4-F_4	1,4-$(CH_3O)_2$	1,4-$(CH_3)_2$	1,2,3,4-Cl_4
ap-**5**	15	20	16	31	32
6	70	64	34	6	7
7	—	16	43	55	47
ap-**8**	15	—	—	—	—
ap-**4**	Trace	Trace	7	8	14

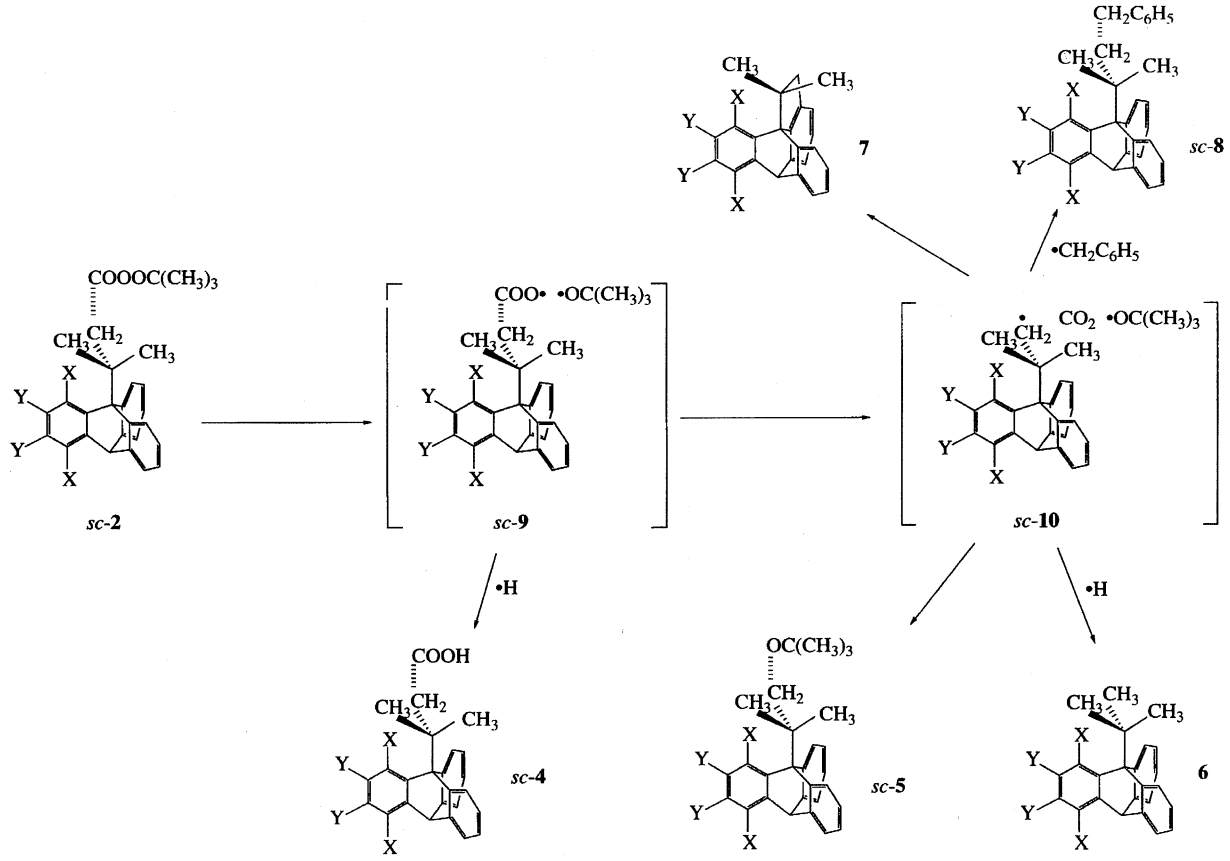
Table 10. Product Distributions (%) in Thermolyses of *t*-Butyl *sc*-Peroxyesters (*sc*-**2**)

Substituents	H	1,2,3,4-F_4	1,4-$(CH_3O)_2$	1,4-$(CH_3)_2$[a)]	1,2,3,4-Cl_4
sc-**5**	15	11	15	10	30
6	70	78	77	—	25
7	—	11	8	—	16
sc-**8**	15	—	—	—	21
sc-**4**	Trace	Trace	Trace	Trace	8

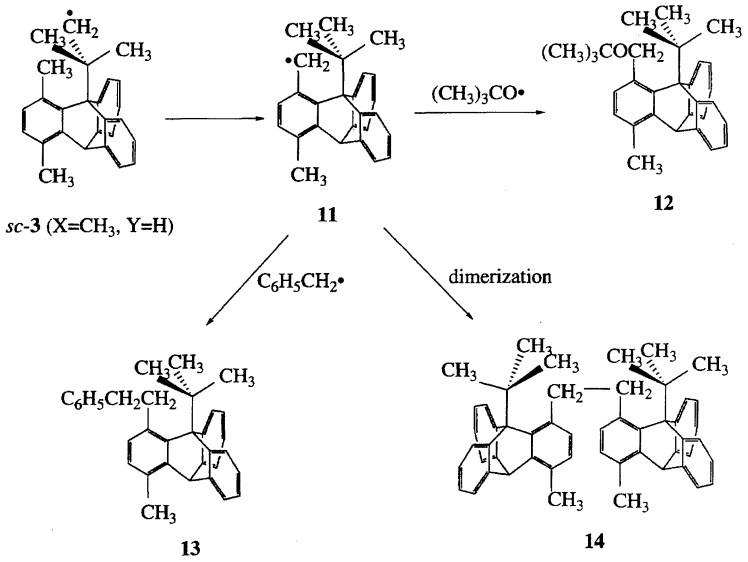
a) In addition, trace of compound **12**, 62% compound **13**, and 28% compound **14** were obtained.



Scheme 3.



Scheme 4.



Scheme 5.

Y=H) to the benzylic radical **11** requires energy of activation.

After rearrangement of the radical **3** to **11**, which is stable because of steric protection and benzylic nature, **11** can survive long enough to go out of its cage and can produce the dimer **14**. Or else, it reacts with benzyl radical produced from the solvent to colligate to produce **13**. The poor yield of the 1-*t*-butoxymethyl compound **12** is attributed to other reactions of the *t*-butoxyl radical, such as hydrogen abstraction before moving closely to the benzylic radical center. This is because, although the lifetime of the *t*-butoxyl radical in the gas phase is known to be rather long (log *A* 14.1 s^{-1}, E_a 15.3 kcal mol^{-1}; 1 cal = 4.184 J),[25] hydrogen abstraction by the *t*-butoxyl radical is a faster reaction than decomposition of itself.[26—29]

Comparison of the Decompositions of Compounds 1 and 2 (X = CH_3, Y = H). Although radical reactions, in which radicals are generated in various ways, are to the first approximation assumed to be the same, they may react in a different way following the ways of generation. Especially because the present work provides data for the radicals generated from the peroxyesters and we have reported radical decompositions of the 2(1*H*)-thioxo-1-pyridyl esters **1** of the same carboxylic acid, the comparison of the data will lead us to get further insight into the radical reactions. The results of thermolyses of these esters for comparison are compiled in Table 11. Incidentally, the rates of decompositions of the peroxyesters were much larger than those of the 2(1*H*)-thioxo-1-pyridyl ester (**1**), because the half life of the peroxyesters (**2**) were ca. 40 min, whereas compound **1** was completely decomposed at 110 °C after 18 h.

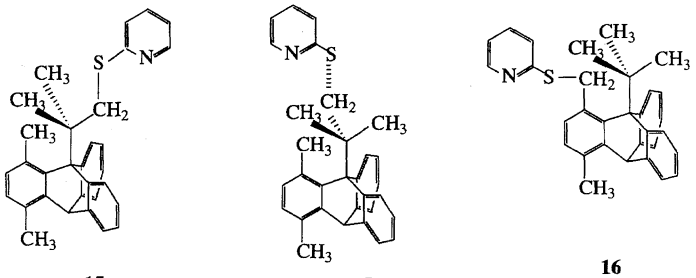
We can point out several differences as well as similarities between the two compounds. Here, we compare the product distributions by taking that products, which possess the same skeleton and only one difference is that a substituent is either a *t*-butoxy group from **2** or a 2-pyridylthio group from **1**, are the same.

Let us begin with the comparison of the results of the *ap* compounds. The main product from both *ap*-**1** and *ap*-**2** is **7**. However, the carboxylic acid *ap*-**4** is more abundantly formed from *ap*-**1**, whereas both yields of *ap*-**5** and **6** are increased in the products from *ap*-**2**. We postulate that a radical produced in the cage (**9**) as a pair with a thio compound (radical) is stabilized with respect to other pairs. Then the results are explained in the following ways.

Table 11. Comparison of Thermolyses of *t*-Butyl *sc*-3-(1,4-Dimethyl-9-triptycyl)methylperoxybutanoate (**2**) and 2(1*H*)-Thioxo-1-pyridyl *sc*-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoate (**1**) in Toluene at 120 °C (Product Distribution/%)

Product	**4**[a]	**5** (or **15**)[a]	**6**	**7**	**12** (or **16**)	**13**	**14**
from *ap*-**1**[b]	22	7	—	64	—	—	—
from *ap*-**2**	8	31	6	55	—	—	—
from *sc*-**1**[b]	15	—	—	—	70	—	11
from *sc*-**2**	Trace	10	—	—	Trace	62	28

a) It should be taken that the *ap* isomer affords the *ap* isomer of these compounds and the *sc* isomer the *sc* products. b)Thermolysis was carried out at 110 °C. In addition, 1,4-dimethyl-9-(1-methyl-1*E*-propenyl)triptycene was detected in 8 and 3% yields from *ap*- and the *sc*-**1**, respectively. The data are taken from Ref. 2.



ap-**15** *sc*-**15** **16**

Scheme 6.

Because the radical pair (*ap*-**9** or *ap*-**10**) produced from *ap*-**2** is less stable than that produced from *ap*-**1**, it has a higher tendency of abstracting a hydrogen to produce **6** or of colligating with the counterpart to produce *ap*-**5** than the case from *ap*-**1**. The relatively high yield of *ap*-**4** from *ap*-**1** with respect to that from *ap*-**2** is another piece of evidence for the lengthened lifetime of the carboxyl radical. Due to stability of the thio radical, the yield of *ap*-**15** is decreased relative to that of *ap*-**5** (Scheme 6). The decrease in the yield of **7** from the peroxyester relative to that of **7** from the thioxopyridyl ester can also be attributed to the stability of the radical pair: The radical pair involving the thio radical is stable and tends to react intramolecularly in the cage rather than intermolecularly.

The results of the *sc*-compounds also show interesting differences. Firstly, although the *t*-butyl compound **6** is not found from either *sc*-**2** or *sc*-**1**, *sc*-**2** gave 10% of the colligation product in the cage, whereas *sc*-**1** did not give such a product. In addition, *sc*-**1** afforded *sc*-**4** more abundantly than *sc*-**2**. Secondly the products derived after rearrangement are more abundant from *sc*-**2** than from *sc*-**1**. The colligation product **13** from benzyl and 9-*t*-butyl-4-methyl-1-triptycylmethyl radicals is abundant from the *sc*-peroxyester **2** but the compound of this type is not formed from *sc*-**1**. The recombination product from radical **11** with *t*-butoxyl is found only in a trace amount, but this type of compound, 9-*t*-butyl-1-[(2-pyridylthio)methyl]triptycene (**16**) which is listed together in the column of **12**, is the main product from *sc*-**1**.

We wish to attribute the results again to the stabilization of the initial radicals by the thio compound as well as the stability of thio radicals relative to the *t*-butoxyl radical. Namely, in the solvent cage, the carboxyl radical is initially formed together with *t*-butoxyl radical or 2-pyridylthio radical from *sc*-**2** or *sc*-**1**, respectively. These radicals **9** seem to be stabilized when the thio compound is present: The high yields of the carboxylic acid from **1** can be attributed, as was the case of *ap*-isomer as well, to the extended lifetime of the carboxyl radical, whose chance of hydrogen abstraction from the solvent is increased. When carbon dioxide is lost from the carboxyl radical, then there is a pair of alkyl radical **3** and *t*-butoxyl radical (**10**) or 2-pyridylthio radical. Colligation between the radical *sc*-**3** and the thio radical is also slow because the latter is stable. As the consequence, the radical pair of the alkyl radical **3** with the thio radical tends to undergo hydrogen migration rather than to produce the colligation product (*sc*-**15**) corresponding to *sc*-**5** and/or hydrogen abstraction to produce **6** with respect to the case of **3** and the *t*-butoxyl radical pair.

The second difference observed is also caused by the difference in stabilities of the radical pairs as well as the difference in lifetimes of *t*-butoxyl and the thio radicals. The *t*-butoxyl radical will decompose or abstract hydrogen before reaching the benzylic position of **11**. Thus compound **12** was formed in only a trace amount. Instead, because of the abundant presence of benzyl radical, the radical **11** gives **13** in a high yield. In contrast, the thio radical will survive until it reaches the radical site in **11**, where it colligates with **11** to produce 9-*t*-butyl-4-methyl-1-(2-pyridylthiomethyl)-triptycene (**16**). The yield of dimer **14** seems to be affected by various factors which are not well known at present but **14** should be formed in competition with other compounds **12** and **13**.

Experimental

The product distribution was determined by ^{1}H NMR spectra, which were measured with use of a Varian Gemini 300 machine that operated at 300.1 MHz, before separation of the products. The product ratios shown in Tables 9 and 10 are averages of three runs. Identification of the products was carried out by comparing the ^{1}H NMR spectra with those of an authentic specimen, when known, or by elemental analyses together with ^{1}H NMR spectra and/or independent syntheses, when unknown. Melting points are not corrected.

9-(1,1-Dimethyl-3-butenyl)triptycene. To a boiling solution of 1.80 g (6.91 mmol) of 9-(1,1-dimethyl-3-butenyl)anthracene,[30] and 0.92 mL (6.9 mmol) of isopentyl nitrite in 32 mL of dichloromethane, was slowly added simultaneously from two separatory funnels a solution of 1.7 g (12 mmol) of anthranilic acid in 17 mL of acetone and that of 2.5 mL (18 mmol) of isopentyl nitrite in 17 mL of acetone. After completion of the addition, the mixture was further heated under reflux for 1 h and cooled. The volatile materials were evaporated and the residue was separated by chromatography on silica gel with hexane eluent. The desired product was obtained in 39% yield, mp 146—148 °C after recrystallization from hexane–dichloromethane. Found: C, 92.61; H, 7.30%. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19%. ^{1}H NMR ($CDCl_3$) δ = 2.06 (6H, s), 3.34 (2H, d, J = 7.3 Hz), 5.24—5.29 (2H, m), 5.30 (1H, s), 6.24—6.33 (1H, m), 6.94—7.02 (6H, m), 7.33—7.40 (3H, m), 7.74—7.79 (3H, m).

3-Methyl-3-(9-triptycyl)butanal. A solution of 302 mg (0.493 mmol) of 9-(1,1-dimethyl-3-butenyl)triptycene, 100 mg (0.898 mmol) of trimethylamine oxide dihydrate, and 18 μL of pyridine in 15 mL of *t*-butyl alcohol and 4.5 mL of water was heated under reflux for 2 h with 14 mg of osmium tetraoxide. The mixture was treated with 20% aqueous sodium hydrogensulfite and

extracted with ether. The extracts were dried and evaporated. The residue (314 mg) was dissolved in 15 mL of THF and stirred for 2 h at room temperature with 289 mg (1.27 mmol) of periodic acid dihydrate and 5.0 mL of water. The product was treated in the usual manner and then purified by chromatography on silica gel with 1 : 1 hexane–dichloromethane eluent. The yield was 55%. Mp 169—170 °C. HRMS(FAB): Found: *m/z* 339.1718. Calcd for $C_{25}H_{23}O$: (M+1), 339.1749. ^{1}H NMR ($CDCl_3$) δ = 2.27 (6H, s), 3.70 (2H, d, J = 2.7 Hz), 5.26 (1H, s), 6.97—7.00 (6H, m), 7.36—7.41 (3H, m), 7.67—7.72 (3H, m), 10.24 (1H, t, J = 2.7 Hz).

3-Methyl-3-(9-triptycyl)butanoic Acid. To a solution of 349 mg (0.534 mmol) of the aldehyde and 54 μL (0.69 mmol) of 30% aqueous hydrogen peroxide in 21 mL of THF, was slowly added a solution of 90 mg (0.80 mmol) of 80% sodium chlorite and the mixture was stirred for a further 3.5 h. The mixture was quenched with aqueous sodium hydrogensulfite and acidified with hydrochloric acid. The mixture was extracted with ether and the extracts were dried over anhydrous magnesium sulfate. This compound was directly used for the next reaction. The following ^{1}H NMR data were recorded ($CDCl_3$, δ = 2.27 (6H, s), 3.64 (2H, s), 5.30 (1H, s), 6.97—7.03 (6H, m), 7.36—7.42 (3H, m), 7.74—7.77 (1H, m), 7.80—7.83 (2H, m). The signal due to the proton in the carboxyl group was not found. Instead the signal due to water at ca. 1.56 ppm was broad.

***t*-Butyl 3-Methyl-3-(substituted 9-triptycyl)peroxybutanoates (2).** The general method of syntheses of these compounds is described by taking the case of the unsubstituted compound. The methods of preparation of the corresponding carboxylic acids with substituents are described elsewhere.[30,31]

A solution of 200 mg (0.564 mmol) of 3-methyl-3-(9-triptycyl)-butanoic acid in 20 mL of benzene was mixed with 0.50 mL (5.8 mmol) of oxalyl dichloride and the whole was stirred for 2 h at room temperature. The solvent and the unreacted oxalyl dichloride were evaporated in vacuo; then the residue was mixed with ice-cooling with a solution (3.8 mL or 19 mmol) of *t*-butyl hydroperoxide in dichloromethane, which was prepared by the Sharpless method,[32] and 1.5 mL (19 mmol) of dry pyridine was added. The mixture was stirred for 1 h at 0 °C for 24—48 h. After the reaction was found to be over by TLC, the mixture was treated with 1 M hydrochloric acid (1 M = 1 mol dm^{-3}) and the organic layer was separated. The solvent was removed after drying over anhydrous magnesium sulfate and the residue was purified by preparative TLC (silica gel, 4 : 1 hexane–dichloromethane eluent) and then recrystallization from hexane–dichloromethane or hexane–THF.

***t*-Butyl 3-Methyl-3-(9-triptycyl)peroxybutanoate (X = Y = H).** Mp 144—152 °C (decomp). Yield 77%. Found: C, 81.92; H, 7.13%. Calcd for $C_{29}H_{30}O_3$: C, 81.66; H, 7.09%. ^{1}H NMR ($CDCl_3$) δ = 1.44 (9H, s), 2.24 (6H, s), 3.57 (2H, s), 5.25 (1H, s), 6.96—7.04 (6H, m), 7.36—7.41 (3H, m), 7.73—7.80 (3H, m).

***t*-Butyl 3-Methyl-3-(1,2,3,4-tetrafluoro-9-triptycyl)peroxybutanoate (X = Y = F).** *ap*-Form, mp 146—154 °C (decomp). Yield 79%. Found: C, 69.62; H, 5.37%. Calcd for $C_{29}H_{26}F_4O_3$: C, 69.87; H, 5.26%. ^{1}H NMR ($CDCl_3$) δ = 1.43 (9H, s), 2.17 (6H, d, J = 8.5 Hz), 3.52 (2H, s), 5.70 (1H, d, J = 0.7 Hz), 7.08—7.11 (4H, m), 7.44—7.46 (2H, m), 7.83—7.85 (2H, m). *sc*-Form, mp 138—147 °C (decomp). Yield 88%. Found: C, 70.04; H, 5.29%. Calcd for $C_{29}H_{26}F_4O_3$: C, 69.87; H, 5.26%. ^{1}H NMR ($CDCl_3$) δ = 1.43 (9H, s), 2.15 (3H, d, J = 7.9 Hz), 2.23 (3H, s), 3.35 and 3.59 (2H, ABq, J = 14.9 Hz), 5.70 (1H, s), 7.05—7.11 (4H, m), 7.41—7.45 (2H, m), 7.81—7.89 (1H, m), 7.90—7.91 (1H, m).

***t*-Butyl 3-Methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)peroxybutanoate (X = Y = Cl).** *ap*-Form, mp 154—158 °C (decomp). Yield 85%. Found: C, 61.47; H, 4.64%. Calcd for $C_{29}H_{26}Cl_4O_3$: C, 61.72; H, 4.64%. ^{1}H NMR ($CDCl_3$) δ = 1.40 (9H, s), 2.47 (6H, s), 3.50 (2H, s), 6.09 (1H, s), 7.10—7.12 (4H, m), 7.46—7.49 (2H, m), 7.89—7.93 (2H, m). *sc*-Form, mp 150—155 °C (decomp). Yield 76%. Found: C, 61.67; H, 4.72%. Calcd for $C_{29}H_{26}Cl_4O_3$: C, 61.72; H, 4.64%. ^{1}H NMR ($CDCl_3$) δ = 1.43 (9H, s), 2.22 (3H, s), 2.42 (3H, s), 3.76 and 4.15 (2H, ABq, J = 15.4 Hz) 6.09 (1H, s), 7.07—7.12 (4H, m), 7.43—7.49 (2H, m), 7.90—7.93 (1H, m), 7.98—8.01 (1H, m).

***t*-Butyl 3-(1,4-Dimethoxy-9-triptycyl)-3-methylbutanoate (X = CH_3O, Y = H).** *ap*-Form, mp 214—227 °C (decomp). Yield 93%. Found: C, 76.35; H, 7.24%. Calcd for $C_{31}H_{34}O_5$: C, 76.52; H, 7.04%. ^{1}H NMR ($CDCl_3$) δ = 1.42 (9H, s), 2.22 (6H, s), 3.53 (2H, s), 3.73 (3H, s), 3.81 (3H, s), 5.89 (1H, s), 6.58 and 6.63 (2H, ABq, J = 9.0 Hz), 6.99—7.02 (4H, m), 7.41—7.43 (2H, m), 7.82—7.85 (2H, m). *sc*-Form, mp 150—157 °C (decomp). Yield 82%. Found: C, 76.72; H, 7.09%. Calcd for $C_{31}H_{34}O_5$: C, 76.52; H, 7.04%. ^{1}H NMR ($CDCl_3$) δ = 1.43 (9H, s), 2.18 (3H, s), 2.20 (3H, s), 3.60 and 4.04 (2H, ABq, J = 15.0 Hz), 3.78 (3H, s), 3.82 (3H, s), 5.90 (1H, s), 6.59 and 6.66 (2H, ABq, J = 9.0 Hz), 6.96—7.02 (4H, m), 7.37—7.44 (2H, m), 7.80—7.83 (1H, m), 7.86—7.89 (1H, m).

***t*-Butyl 3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoate (X = CH_3, Y = H).** *ap*-Form, mp 144—151 °C (decomp). Yield 75%. Found: C, 81.67; H, 7.57%. Calcd for $C_{31}H_{34}O_3$: C, 81.90; H, 7.54%. ^{1}H NMR ($CDCl_3$) δ = 1.40 (9H, s), 2.40 (6H, s), 2.49 (3H, s), 2.66 (3H, s), 3.58 (2H, s), 5.59 (1H, s), 6.75 (2H, s), 7.00—7.02 (4H, m), 7.37—7.39 (2H, m), 7.82—7.84 (2H, m). *sc*-Form, mp 141—150 °C (decomp). Yield 67%. Found: C, 81.92; H, 7.67%. Calcd for $C_{31}H_{34}O_3$: C, 81.90; H, 7.54%. ^{1}H NMR ($CDCl_3$) δ = 1.42 (9H, s), 2.29 (3H, s), 2.32 (3H, s), 2.53 (3H, s), 2.72 (3H, s), 3.67 and 3.85 (2H, ABq, J = 16.1 Hz), 5.60 (1H, s), 6.79 (2H, s), 6.98—7.03 (4H, m), 7.34—7.40 (2H, m), 7.82—7.89 (2H, m).

Thermolyses of the Peroxyesters. The peroxy compound (20 mg) was dissolved in 1.0 mL of dried and distilled toluene and placed in an NMR sample tube. The inside of the tube was thoroughly degassed and filled with argon. The tube was sealed and placed in a bath which was heated at 120 °C for 10 h. After cooling, the tube was opened, the solvent removed, and the residue submitted to TLC and HPLC, when necessary. After identifying the products by comparing the ^{1}H NMR spectra with authentic samples, the product distribution was determined by comparing the intensities of ^{1}H NMR signals. The results are shown in Tables 9 and 10. In addition to these compounds, 1,2-diphenylethane was always found in the product mixture, the yield being about half of those of 9-*t*-butyltriptycene derivatives.

9-*t*-Butyltriptycene,[17] 9-*t*-butyl-1,2,3,4-tetrachlorotriptycyene,[17] 9-*t*-butyl-1,2,3,4-tetrafluorobutyltriptycene,[33] and 9-*t*-butyl-1,4-dimethyltriptycene[2] are described in the literature and their ^{1}H NMR spectra were used for identification and analyses.

9-*t*-Butyl-1,4-dimethoxytritpycene (6: X = CH_3O, Y = H). To a boiling solution of 17.0 mmol of 9-*t*-butylanthracene[34] and 17.0 mmol of isopentyl nitrite in 300 mL of dichloromethane, were added simultaneously from two dropping funnels a solution of 34.0 mmol of 3,6-dimethoxyanthranilic acid[35] in 100 mL of acetone and a solution of 5.0 mL of isopentyl nitrite in 50 mL of dichloromethane in 3 h. The whole mixture was refluxed for a further 1 h. The solvents were evaporated and the residue was submitted to chromatography on silica gel with a 4 : 1 hexane–dichloromethane eluent. The product was finally purified by recrystallization from dichloromethane–hexane, mp 248—249 °C. The yield was 22%. Found: C, 84.34; H, 7.15%. Calcd for $C_{26}H_{26}O_2$: C, 84.29; H,

7.07%. ^{1}H NMR ($CDCl_3$) δ = 2.04 (3H, s), 2.08 (6H, s), 3.72 (3H, s), 3.81 (3H, s), 5.87 (1H, s), 6.57 and 6.61 (2H, ABq, J = 8.9 Hz), 6.95—6.98 (4H, m), 7.38—7.40 (2H, m), 7.86—7.89 (2H, m).

Substituted 9-(2-*t*-butoxy-1,1-dimethylethyl)triptycenes (**5**)[36] and substituted 1,1-dimethyl-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylenes (**7**)[37] were described in the literature. The ^{1}H NMR spectra of these products were identical with those reported.

9-(2-*t*-Butoxy-1,1-dimethylethyl)triptycene (5: X = Y = H). This compound was purified by HPLC (20 : 1 hexane–ethyl acetate eluent), after TLC (4 : 1 hexane–dichloromethane eluent) which separated a mixture of this compound with 9-(1,1-dimethyl-3-phenylpropyl)triptycene from **4** and **6**. Mp 210—212 °C. HRMS (FAB) Found: *m/z* 382.2292. Calcd for $C_{28}H_{31}O$: (M + 1), 382.2297. ^{1}H NMR ($CDCl_3$) δ = 1.29 (9H, s), 2.07 (6H, s), 4.21 (2H, s), 5.24 (1H, s), 6.94—7.01 (6H, m), 7.35—7.39 (3H, m), 7.74—7.77 (2H, m), 7.80—7.83 (1H, m).

9-(1,1-Dimethylpropyl-3-phenyl)triptycene (8: X=Y=H). A solution of phenylmagnesium bromide was prepared from 118 mg (4.85 mmol) of magnesium, 761 mg (4.85 mmol) of bromobenzene, and 30 mL of ether and was added to 92.0 mg (0.272 mmol) of the aldehyde. The mixture was heated under reflux for 30 min and treated with aqueous ammonium chloride. The organic layer was separated and the products were treated in a usual manner. The desired compound was obtained in 61% yield and was purified by recrystallization from hexane–dichloromethane, mp 188.5—189.5 °C. This compound was used for the next reaction. ^{1}H NMR ($CDCl_3$) δ = 2.00 (1H, d, J = 1.9 Hz), 2.22 (3H, s), 2.34 (3H, s), 2.87 (1H, A of ABX, J_{AB} = 15.4, J_{AX} = 0 Hz), 3.02 (1H, B of ABX, J_{AB} = 15.4, J_{BX} = 9.2 Hz), 5.22 (1H, s), 5.45—5.48 (1H, m), 6.93—7.01 (6H, m), 7.18—7.39 (6H, m), 7.48 (2H, d, J = 7.0 Hz), 7.62—7.65 (1H, m), 7.84—7.87 (1H, m), 8.00—8.03 (1H, m). The alcohol (69.4 mg) thus obtained was dissolved in 5 mL of ethanol and shaken under a hydrogen atmosphere for 17 h with 41.7 mg of 5% palladium on carbon and a drop of concentrated hydrochloric acid. The catalyst was removed by filtration, the solvent removed in vacuo, and the residue taken up in ether. The solution was washed with aqueous sodium hydrogencarbonate and dried. The product was purified by chromatography on silica gel with hexane eluent. The analytical sample was obtained by recrystallization from hexane–dichloromethane, mp 185.5—186.5 °C. The yield was 64%. Found: C, 92.95; H, 7.09%. Calcd for $C_{31}H_{28}$: C, 92.95; H, 7.05%. ^{1}H NMR ($CDCl_3$) δ = 2.15 (6H, s), 2.83—2.89 (2H, m), 3.10—3.16 (2H, m), 5.23 (1H, s), 6.95—6.99 (6H, m), 7.16—7.30 (5H, m), 7.35—7.39 (3H, m), 7.77—7.82 (3H, m).

***sc*-1,2,3,4-Tetrachloro-9-(1,1-dimethyl-3-phenylpropyl)-triptycene (*sc*-8: X = Y = Cl).** This compound was similarly prepared from the *sc*-tetrachloro aldehyde,[31] of which *ap* and *sc* isomers were found easily separable by HPLC (2 : 1 hexane–dichloromethane eluent, flow rate 5.00 mL min^{-1}, pressure 63.0 kg cm^{-2}, retention times being 40 and 44 min for *sc* and *ap*, respectively). The yield of the alcohol was 40% as a mixture of diastereomers, of which distribution was found to be ca. 2 : 1. No attempt was made at any assignment of the stereochemistry. Hydrogenolysis of the diastereomeric mixture afforded the desired compound in 61% yield. Recrystallization from hexane–dichloromethane afforded a pure sample, mp 202.0—202.5 °C. Found: C, 69.28; H, 4.53%. Calcd for $C_{31}H_{24}Cl_4$: C, 69.16; H, 4.49%. ^{1}H NMR ($CDCl_3$) δ = 2.13 (3H, s), 2.23 (3H, s), 2.89—3.01 (2H, m), 3.10—3.20 (2H, m), 6.07 (1H, s), 7.00—7.09 (5H, m), 7.20—7.32 (4H, m), 7.42—7.44 (2H, m), 7.96—8.03 (2H, m).

1-(*t*-Butoxymethyl)-9-*t*-butyl-4-methyltriptycene (12). A solution of 19 mg (98 mmol) of silver tetrafluoroborate was mixed with a solution of 30 mg (81 mmol) of 9-*t*-butyl-1-(chloromethyl)-4-methyltriptycene[6] in 2 mL of *t*-butyl alcohol and the mixture was stirred for 2 h at room temperature. Silver chloride was removed by filtration and the solvent was evaporated. The residue was fractionated by TLC with 1 : 1 hexane–dichloromethane. The desired compound, mp 186.0—186.5 °C, was obtained in 58% yield. The analytical sample was obtained by recrystallization from hexane–dichloromethane. Found: C, 87.58; H, 8.39%. Calcd for $C_{29}H_{34}O$: C, 87.76; H, 8.34%. ^{1}H NMR ($CDCl_3$) δ = 1.30 (9H, s), 2.08 (3H, s), 2.24 (6H, s), 2.50 (3H, s), 4.68 (2H, s), 5.56 (1H, s), 6.86 and 7.06 (2H, ABq, J = 7.9 Hz), 6.95—6.98 (4H, m), 7.32—7.35 (2H, m), 7.88—7.91 (2H, m). 9-*t*-Butyl-1-(hydroxymethyl)-4-methyltriptycene, which was identical with the authentic specimen,[38] was formed also in this reaction in 14% yield.

9-*t*-Butyl-4-methyl-1-(2-phenylethyl)triptycene (13). A Grignard reagent was prepared from 500 mg (22.6 mmol) of magnesium, 2.53 g (20.0 mmol) of benzyl bromide, and 25 mL of THF and was added to a solution of 50.0 mg (0.134 mmol) of 9-*t*-butyl-1-chloromethyl-4-methyltriptycene in 2 mL of THF. The mixture was stirred at room temperature for 3 h and then heated under reflux for 1 h. The mixture was decomposed with a saturated aqueous solution of ammonium chloride and the organic layer was separated. After the usual treatment, the products were separated by TLC (8 : 1 hexane–dichloromethane eluent), which afforded 35% unreacted material, a mixture of 28% **13** and 13% 9-*t*-butyl-1,4-dimethyltriptycene,[2] and 8% 1,2-bis(9-*t*-butyl-4-methyl-1-triptycyl)ethane,[2] R_f's being 0.60, 0.65, and 0.40, respectively. The desired compound was obtained by HPLC (10 : 1 hexane–ether eluent, flow rate 15 mL min^{-1}) from the mixture and then purified by recrystallization from hexane, mp 181—182 °C. Found: C, 92.71; H, 7.61%. Calcd for $C_{33}H_{32}$: C, 92.47; H, 7.53%. ^{1}H NMR ($CDCl_3$) δ = 2.07 (3H, s), 2.26 (6H, s), 2.53 (3H, s), 2.81—2.86 (2H, m), 3.31—3.36 (2H, s), 5.60 (1H, s), 6.85 and 7.32 (2H, ABq, J = 7.5 Hz), 6.84—7.03 (5H, m), 7.23—7.28 (4H, m), 7.36—7.39 (2H, m), 7.89—7.92 (2H, m).

Determination of Rates of Decomposition. A solution of a peroxyester was prepared by dissolving 10 mg of the peroxyester in 0.5 mL of toluene-d_8 which was thoroughly dried. *t*-Butylbenzene (the same molar amount with the substrate) was added to the solution which was placed in an NMR sample tube. The oxygen was removed by the freeze-thaw method and the tube was sealed after filling with argon gas. The tube was immersed in a thermostat which was heated at 120 °C and the decrease in the signal intensity due to *t*-butyl protons of the substrate was measured with the reference peak intensity of *t*-butylbenzene with about 5 minute intervals, 6—10 points being obtained for one run. The data points obeyed the first order kinetics with correlation coefficients of 0.996—0.998. The data are shown in Table 8.

X-Ray Crystallography. Crystals suitable for X-ray crystallography were grown from dichloromethane–hexane. X-Ray data were obtained on a Rigaku AFC7R four circle diffractometer with Cu $K\alpha$ radiation (λ = 1.54178 Å). The scan mode was the 2θ method in the range of $2\theta < 120°$, the scan rate being 10, 16, 16, and 12° min^{-1} for the unsubstituted, methoxy, methyl, and chloro compounds, respectively. The scan range was calculated by $A° + 0.35°$ tan θ, where the value A is given in Table 12. The weak reflections were scanned three times. The structures were solved by the direct method and refined by the full-matrix least-square method by using the teXsan program. Anisotropic and isotropic thermal parameters were employed for non-hydrogen and hydrogen atoms, respectively. Some hydrogen atoms were refined but most of them

Table 12. Crystal Data of *t*-Butyl *ap*-3-Methyl-3-(substituted 9-triptycyl)peroxybutanoates (*ap*-**2**)

Substituents	H	1,4-$(CH_3O)_2$	1,4-$(CH_3)_2$	1,2,3,4-Cl_4
Empirical formula	$C_{29}H_{30}O_3$	$C_{31}H_{34}O_5$	$C_{31}H_{34}O_3$	$C_{29}H_{26}Cl_4O_3$
Formula weight	426.55	486.61	454.61	564.33
Crystal dimension/mm^3	$0.30\times0.25\times0.35$	$0.20\times0.20\times0.30$	$0.50\times0.30\times0.10$	$0.08\times0.57\times0.99$
Crystal system	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*Pbca*
a/Å	9.877(2)	9.852(2)	9.673(1)	20.138(7)
b/Å	13.744(2)	15.498(3)	15.516(1)	17.995(7)
c/Å	9.437(1)	9.390(1)	8.561(1)	14.584(8)
α/°	96.34(1)	99.13(1)	97.230(9)	90
β/°	104.53(1)	110.31(1)	105.473(9)	90
γ/°	72.644(9)	77.10(1)	87.762(9)	90
V/Å^3	1182.6(3)	1305.6(4)	1228.4(2)	5284(3)
Z	2	2	2	8
D_c/g cm^{-3}	1.198	1.238	1.229	1.418
μ(Cu $K\alpha$)/cm^{-1}	5.99	6.65	6.07	43.15
No. of reflections	3755	4133	3908	4388
No. of observations	2953	3332	3417	2956
A value	1.57	0.63	0.94	1.42
R	0.065	0.053	0.050	0.068
R_w	0.054	0.054	0.065	0.066

were included in fixed positions. An empirical absorption correction based on azimuthal scans of several reflections was applied. This resulted in transmission factors ranging from 0.26 to 1.00 and 0.90 to 1.00, for the chloro and the methyl compounds, respectively, but the azimuthal scans indicated no need of absorption corrections for the unsubstituted and the methoxy compounds. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The function minimized was $\sum[w(|F_o|-|F_c|)^2]$ where $w=(\sigma_c^2|F_o|)^{-1}$. Additional crystal and analysis data are listed in Table 12.

The complete F_o-F_c data together with relevant data including bond distances and bond angles have been deposited as Document 70004 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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16) We believe taking the average of two distances is more appropriate than discussing the respective nonbonding distances for the following reasons. The first is that the X-ray structure gives the geometry in the solid state. Under the reaction conditions, the atoms must be in motion with rather large amplitudes. The second is the structure of the radicals produced, which should take sp^2-hybridized structure. Since the radical center is less bulky than the sp^3-hybridized methylene, the distance between the radical center and the *peri*-carbons may be modified because of the reduced steric interactions.

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