*Tetrahedron.* Vol. 30, pp. 2173 to 2181. Pergamon Press 1974. Printed in Great Britain

# SMALL RING COMPOUNDS—XXIX[1]

## THERMAL DECOMPOSITION OF t-BUTYL PER (*TRANS*-2-SUBSTITUTED CYCLOPROPYL) ACETATES

T. SHONO* and I. NISHIGUCHI

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

(*Received in Japan* 14 *December* 1973; *Received in the UK for publication* 1 *February* 1974)

**Abstract**—Three kinds of t-butyl per (*trans*-2-substituted cyclopropyl) acetates (R=H, $CH_3$, $C_6H_5$) were synthesized from the corresponding acyl chlorides and thermally decomposed in cyclohexane to investigate the chemical stability and behaviour of the cyclopropylcarbinyl radical. Clean first-order kinetics were obtained in all of the thermal decomposition reactions. The experimental fact that the decompositoin rates and activation parameters of these three t-butyl peresters are similar to each other may indicate the absence of the ionic character in the transition state suggesting the almost complete homolytic decomposition of these peresters. Although the typical concerted decomposition might be invalid for these peresters in view of the activation parameters, it would be suggested from the product studies that the decomposition of these peresters was characterized by a considerable loss of their acyl-alkyl bonds at the time of the fission of their O—O bonds. The products yielded from the thermal decomposition of t-butyl per (*trans*-2-phenylcyclopropyl) acetate in various hydrogen donating solvents consisted of three hydrocarbons and two t-butyl ethers. The formation of these t-butyl ethers, possibly cage products, was significant.

### INTRODUCTION

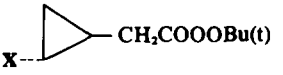
Extensive studies have been applied to elucidate the nature of the cyclopropylcarbinyl radical,[2-4] but the stability and chemical behaviour of this particular radical species, has not been clarified. For instance, in some reactions involving a free radical intermediate at the rate determining step, the formation of cyclopropylcarbinyl radical enhances the reaction rates.[2] Reversely, the similarity in the stability of the cyclopropylcarbinyl radical relative to the other simple alkylcarbinyl radicals has been observed in some other reactions.[3,4]

Furthermore, a clear-cut general explanation for the rate acceleration in the generation of the cyclopropylcarbinyl radical, if any, has not been given. The relief of considerable ring strain brought by the concerted opening of cyclopropane ring might be one of the important driving forces. The charge polarization in the transition state might be another factor to bring about the rate enhancement,[2c,2f] since even a very small degree of charge separation would be sufficient to explain the rate acceleration observed in the radical reactions.[5] Martin and Timberlake[2a] have proposed that a conjugate interaction between cyclopropane ring and a developing radical center may be significant for the stabilization of the cyclopropylcarbinyl radical.

Although the homoallylic rearrangement[6] between the cyclopropylcarbinyl and the allylcarbinyl radicals has been studied extensively, the problem of the electron delocalization in the cyclopropylcarbinyl radical is still pending.

Generally, t-butyl peresters (1) are available to investigate the stability and properties of the radical R·. When oxygen–oxygen and acyl-alkyl bonds in the t-butyl peresters (2, 3, 4) are cleaved synchronously, it may be anticipated to estimate the effect of the 2-substitutents on the cyclopropane ring on the decomposition rates of these peresters and the chemical behaviour of the radicals. Thus, the following three t-butyl per (*trans*-2-substituted cyclopropyl) acetates (2, 3, 4) were synthesized, and thermally decomposed to obtain more informations on the nature of the cyclopropylcarbinyl radical.

RCOOOBu(t)
1




2: X = H
3: X = $C_6H_5$
4: X = $CH_3$

### RESULTS

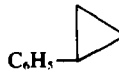
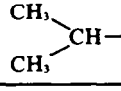
*Synthesis of t-butyl percyclopropylacetates* 2, 3 *and* 4. A series of the peracetates (2, 3 and 4) were synthesized by the usual method from the corresponding acyl chlorides. The structures of these t-butyl peracetates were identified by spectroscopic and elemental analyses (Experimental).

*Kinetic study.* The t-butyl percyclopropyl ace-

tates (2, 3, 4), and t-butyl perisovalerate (5) were thermally decomposed in cyclohexane at 90°, 100° and 110°, and their decomposition rates were determined by the IR technique.[7] The first-order kinetic results are summarized in Table 1. The experimental plots in each run showed a good linear relationship and the Arrhenius plots of their decomposition rates also gave good correlations with 1/T. It thus appeared that the peracetates (2, 3, 4 and 5) decomposed according to the clean first-order kinetics with no complex induced decompositions.

The structures of all of the decomposition products (6, 7, 8, 9 and 10) were identified by spectroscopic and elemental analyses, and some of them were characterized by the comparison of their spectroscopic and gas chromatographic behaviour with those of the authentic samples.

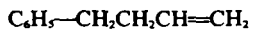
Table 1. Decomposition rates of t-butyl peracetates (2, 3, 4 and 5)[a]

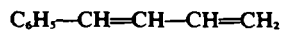
| R | | R—COOOBu(t) k($X10^{-5}$ $sec^{-1}$) 90·0° | 100·0° | 110·0° | $\Delta H^{\neq}$ (kcal/mol) | $\Delta S^{\neq}$[b] (cal/deg) |
|---|---|---|---|---|---|---|
|  | (2) | 2·18 | 7·97 | 23·2 | 33·4 | 11·6 |
|  | (3) | 2·40[c] | 10·9 | 31·1[d] | 32·9 | 10·7 |
|  | (4) | 2·73 | 10·8 | 30·9 | 31·6 | 7·366 |
|  | (5) | 1·17 | 3·95 | 12·5 | 32·0 | 6·54 |

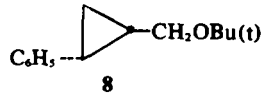
[a] 0·2 mol/l, in cyclohexane.
[b] at 110·0°.
[c] at 89·5°.
[d] at 110·5°

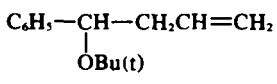
*The products from t-butyl per (trans-2-phenylcyclopropyl) acetate* (3). The t-butyl peracetate (3) was decomposed in various hydrogen-donating solvents at 100° for 24 hr to study the configuration and distribution of the products. The decomposition products consisted of 4-phenylbutene (6), 4-phenylbutadiene (7), *trans*-2-phenylcyclopropylcarbinyl t-butyl ether (8), 4-phenyl-4-t-butoxybutene (9) and 4-phenyl-4-cyclohexyl (or cyclohexenyl) butene (10a or 10b). From the IR analysis of the mixture, the corresponding acid or ester was found only in traces.

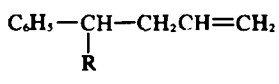
The authentic samples of both unrearranged and rearranged t-butyl ether, 8 and 9, were prepared from the reaction of the corresponding chloride with t-butanol in the mixed solvent of tetrahydrofuran and hexamethylphosphoramide containing sodium hydride. Moreover, both recombination products, 10a and 10b, between phenylallylcarbinyl

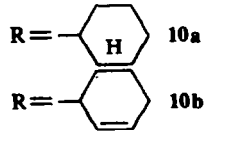

6

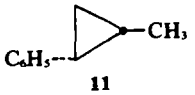

7

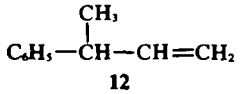

8

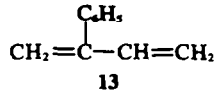

9




10a 10b


11


12


13

radical and cyclohexyl or cyclohexenyl radical were synthesized from the corresponding Gringnard reactions of phenylallylcarbinyl chloride. *trans*-2-Phenyl-1-methylcyclopropane (**11**)[8], 3-phenylbutene (**12**)[9] and 2-phenylbutadiene[10] were also prepared according to the reported literature procedures, though they were not detected in the mixture.

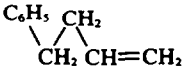
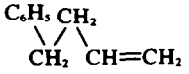
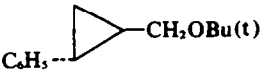
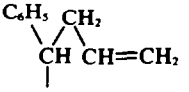
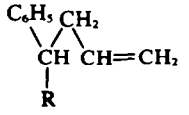
The yield of each product obtained from the decomposition of **3** in such hydrogen-donating hydrocarbons as cyclohexene cyclohexene or 1,4-cyclohexadiene are summarized in Table 2.

nents which may be expected to be formed from the thermal decomposition of the peracetate (**4**).

## DISCUSSION

As is shown in Table 1, the rates and activation parameters of the decomposition of the peresters (**2**, **3** and **4**) were similar to each other. These kinetic results may indicate that the decomposition reactions of these peresters are almost completely homolytic and proceed via a similar transition state, since it was already shown by Schleyer *et al.*[5a] that 2-methyl substitutents in the cyclopropylcarbinyl

Table 2. Yields of decomposition products of t-butyl per (*trans*-2-phenylcyclopropyl) acetate (**3**) in various hydrocarbon solvents[a]

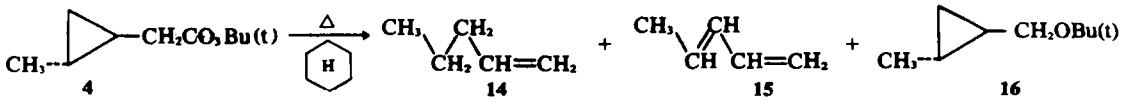
| Products \ Solvents | | H (%) | ⬡ (%) | ⬡ (%) |
|---|---|---|---|---|
|  | (**6**) | 6·5 | 7·4 | 37·5 |
|  | (**7**) | 0·4 | 0·6 | 0·7 |
|  | (**8**) | 2·0 | 2·3 | 1·6 |
|  | (**9**) | 9·8 | 9·8 | 4·7 |
|  | (**10**) | 15·1[b] | 22·8[c] | (1·0)[d] |

[a] 100°, 0·2 mol/l, 24 hours.
[b] R = cyclohexyl (**10a**).
[c] R = cyclohexenyl (**10b**).
[d] R = cyclohexadienyl.

*The Products from t-butyl per (trans-2-methylcyclopropyl) acetate* (**4**).–The thermal decomposition of t-butyl peracetate (**4**) in cyclohexane gave n-pentene (**14**), n-pentadiene-1,3 (**15**) and *trans*-2-methylcyclopropylcarbinyl t-butyl ether (**16**) as main products. Although three or four unidentified components (except for t-butanol, acetone and dicyclohexyl) were present as minor products, the IR and gas chromatographic analyses of the mixture indicated the absence of 3-methylbutene-1, isoprene and any carbonyl compocation brought a considerable rate enhancement (8 ~ 10 times) relative to the parent nonsubstituted cation in the solvolytic reactions.

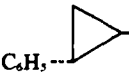
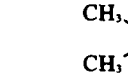
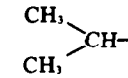
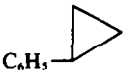
Unexpectedly, the activation parameters obtained for the thermal decomposition of **2**, **3** and **4** would not imply the typical concerted decomposition.[7,11] The following experimental results, however, do not suggest the typical nonconcerted decomposition.

(1) The corresponding acids and esters, typical products of the nonconcerted decomposition of




4 14 15 16

Table 3. Half-lives of t-butyl peresters RCOOOBu(t) (at 60°)

| R | Half life, $t_{1/2}$ (min) | $\Delta H^{\neq}$ (kcal/mol) | $\Delta S^{\neq}$ (cal/deg) |
|---|---|---|---|
|  | [a] $4.18\times10^{4}$ | 33·4 | 11·6[a] |
|  | [a] $2.83\times10^{4}$ | 32·9 | 10·9[a] |
|  | [a] $2.12\times10^{4}$ | 31·6 | 7·4[a] |
| $CH_3$ | [c] $5.0\times10^{5}$ | 38 | 17 [b] |
|  | [c] $1.0\times10^{4}$ | 31·8 | 9·4[c] |
|  | [a] $5.80\times10^{4}$ | 32·0 | 6·7[a] |
|  | [f] $1.10\times10^{5}$ | 32·5 | 6·9[b] |
| $C_6H_5$ | [c] $3.0\times10^{5}$ | 33·5 | 7·8[d] |
| $C_6H_5CH_2$ | [c] 1700 | 28·7 | 3·9[b] |

[a] In cyclohexane.
[b] In chlorobenzene.
[c] In cumene.
[d] In *p*-chlorotoluene.
[e] H. Minato, *J. Syn. Org. Chem. Japan* **23**, 12 (1965).
[f] Ref 12.
[g] Present study.

peresters,[12] were almost absent in the decomposition products.

(2) The unrearranged t-butyl ethers (**8** and **16**) were obtained as one of the main products in spite of the remarkable tendency of the cyclopropylcarbinyl radical to rearrange to allylcarbinyl radical.[6]

(3) A small rate enhancement was observed for the decomposition of **2**, **3** and **4** against that of t-butyl perisovalerate (**5**).

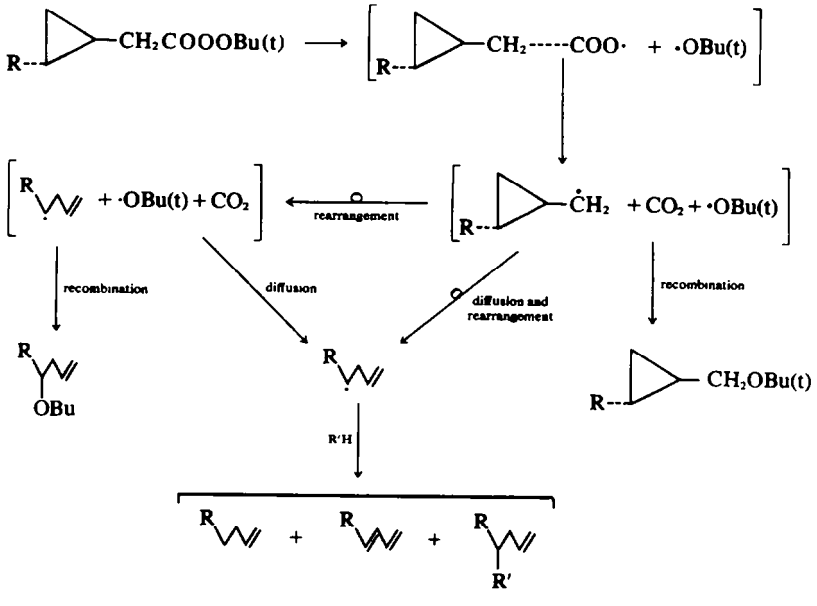
Therefore, it might be postulated as a characteristic of the thermal decomposition of these percyclopropylacetates (**2**, **3** and **4**) that the acyl–alkyl bond becomes considerably loose at the time of the cleavage of the oxygen–oxygen bond and hence the loosing of the former bond does not allow the formation of an acyloxy radical as an intermediate.

The half-lives at 60° and the activation parameters of various t-butyl pereaters are summarized on Table 3. As is shown in Table 3, cyclopropylcarbinyl radicals generated from the peracetates (**2**, **3** and **4**) seem to be not as stable as the radical (e.g., benzyl radical[13]) characterized by the typical concerted decompositoin. The rate constant of the decomposition of t-butyl percyclopropylacetate (**2**) was slightly larger (2 ~ 3 times, at 90° ~ 110°) than that of t-butyl perisovalerate (**5**).

It may also be reasonable that the total yield of hydrocarbons [**6** + **7** + **10**] increased with the increase in the hydrogen-donating ability of the solvents. The negligible formation of 4-phenyl-4-cyclohexadienylbutene would be relationalized by the facile transformation of 1,4-cyclohexadienyl radical to benzene.

The fact is quite noteworthy that the peracetate (**3**) gave unrearranged and rearranged t-butyl ethers (**8** and **9**), and the ratio of the rearranged ether to the unrearranged one (*ca* 3 ~ 5) was almost independent upon the hydrogen-donating ability of the solvents. From the thermal decomposition of 2-methyl substituted peracetate (**4**), *trans*-2-methylcyclopropylcarbinyl t-butyl ether (**16**) was also obtained as one of the main products. The formation of these t-butyl ethers could be explained by several different mechanisms. However, it may be very difficult to elucidate this fact by the hypothesis that the t-butoxy radical once diffused into such

hydrogen-donating solvents recombined with the cyclopropylcarbinyl radical or allylcarbinal radical to give the corresponding t-butyl ether. Moreover, the induced bimolecular decomposition may be denied by the clean first-order kinetics. Therefore, it would be more reasonable to suppose that a solvent cage was an important role in the formation of these t-butyl ethers. Moreover, the similarity of the ratio of the rearranged t-butyl ether (**9**) to the unrearranged one (**8**) in three solvents may also suggest the availability of the solvent cage. Consequently, it would be proposed that in the thermal decomposition of the peracetates (**3** and **4**), the oxygen–oxygen bond was cleaved with the considerable loosing of the acyl–alkyl bond, and some fractions of the unrearranged cyclopropylcarbinyl radical were recombined with the t-butoxy radical in the solvent cage. The facile rearrangement of cyclopropylcarbinyl radical to allylcarbinyl radical in the solvent cage competed with the diffusion of the former radical into solvent. The recombination of the resulting allylcarbinyl radical with the t-butoxy radical in the solvent cage would also compete with their diffusion into solvent (Scheme 2).




The formation of *trans*-2-substituted cyclopropylcarbinyl t-butyl ether (**8** and **16**) in the solvent cage is comparable to the fact that in the solvent cage the stereoconfiguration of radical is retained in spite of the stereoconfigurational instability of the radical.[14] On the other hand, *trans*-2-phenyl-1-methylcyclopropane (**11**), the product formed through the hydrogen-abstraction of the corresponding radical from solvent, was not detected in the reaction mixture. This result would indicate the instability of the cyclopropylcarbinyl radical at the outside of the solvent cage and the remarkable contribution of the solvent cage for the formation of **8** and **16**.

## EXPERIMENTAL

*Synthesis of t-butyl percyclopropylacetate* **2**

(The title peracetate (**2**) was prepared according to a following reaction route.)

*Cyclopropylcarbinyl cyanide.* Into a solution of NaCN (16·0 g; 0·326 mole) in 15 ml water, cyclopropylcarbinyl bromide (22·0 g; 0·163 mole) prepared from the reaction of the corresponding alcohol with $PBr_3$ at acetone-dry ice temp in 62·5% yield, dissolved in 20 ml EtOH was added dropwise with stirring over a period of 15 min. The mixture was stirred under reflux for 4 h. The resulting dark-red mixture was poured into 200 ml water and extracted with three 100 ml portions of ether. The combined ethereal layer was washed with four 10 ml portions of 3:1 $H_2SO_4$ aq in order to remove isonitrile formed as a by-product. The ethereal soln was then neutralized with $NaHCO_3$, washed with two 100 ml portions of water and dried over $MgSO_4$. After the ether was removed, fractional distillation gave 9·3 g of cyclopropylcarbinyl cyanide (Y = 70·6%), b.p. 148 ~ 149° (lit. 147°,[16] 142 ~ 144°[17]), which was found to have the purity of *ca* 79% by the gas chromatographic technique. The NMR spectrum of cyclopropylcarbinyl cyanide showed complex absorption pattern at $\tau$ = 8·70 ~ 9·90 ppm characteristic for the cyclopropane ring protons.

*Cyclopropylacetyl chloride.* Into 100 ml anhyd ether containing cyclopropylacetic acid (7·0 g; 0·07 moles) (prepared from alkali hydrolysis of cyclopropylcarbinyl cyanide with NaOH aq in 76·0% yield), oxalyl chloride (10·1 g; 0·08 moles) was added dropwise at room temp, and the mixture was stirred for one day at room temp.

After the ether was evaporated, fractional distillation gave almost pure cyclopropylacetyl chloride, b.p. 120~121°; yield, 29·1%; NMR ($CCl_4$): $\tau$ = 7·27 (2H, d), 8·60~9·85 (5H, m); (Found: C, 50·85; H, 6·20; Cl, 29·81. $C_5H_7OCl$ requires: C, 50·66; H, 5·95; Cl, 29·90%).

*t-Butyl percyclopropylacetate.* A solun of 15 ml of anhyd ether containing cyclopropylacetyl chloride (2·7 g; 0·023 moles) was added carefully into a solun of 6·18 g (0·068 moles) of t-butyl hydroperoxide and 7·12 g (0·091 moles) of pyridine in 15 ml anhyd ether with vigorous stirring at ice–water temp. The mixture was allowed to stand for 3 days at room temp in the dark, and then poured into 100 ml ice–water. The organic components were extracted with three 30 ml portions of ether, and the combined ethereal layer was washed with 10% $H_2SO_4$ aq, neutralized with 10% $NaHCO_3$ aq and dried over $MgSO_4$. After removal of the drying agent by filtration, the ether and excess t-butyl hydroperoxide were completely removed under reduced pressure at room temp, and the colorless oil was obtained in 68·9% yield, which was found to be the almost pure desired peracetate through spectroscopic and elemental analyses. NMR ($CCl_4$): $\tau$ = 7·78 (2H, d), 8·76 (2H, d), 8·76 (9H, s), 8·70~9·90 (5H, m); IR (neat): 1779 $cm^{-1}$ (>C=O); (Found: C, 62·50; H, 9·65. $C_9H_{16}O_3$ requires: C, 62·76; H, 9·36%).

*Synthesis of t-butyl per* (trans-2-*phenylcyclopropyl*) *acetate* (3). The peracetate 3 was prepared according to the route mentioned for preparation of 2. *trans*-2-Phenylcyclopropylcarbinol was prepared by reduction of the corresponding ethyl ester, obtained by careful fractional distillation of its isomeric mixture, with LAH according to the method reported previously by the authors.[5c]

trans-2-*Phenylcyclopropylcarbinyl chloride.* Into a solun of 800 ml anhyd ether containing *trans*-2-phenylcyclopropylcarbinol (57 g; 0·385 moles) and tri-n-butylamine (93 g; 0·500 moles) $SOCl_2$ (50·0 g; 0·420 moles) was added dropwise with vigorous stirrring at −10°. After addition, the mixture was continously stirred at −10°~−5° for 1h and at room temp 2h. After evaporation of the ether under reduced pressure, the desired chloride was obtained in 91% yield by fractional distillation of the red-brown residue, b.p. 73~74°/4 mm; NMR ($CCl_4$): $\tau$ = 2·86 (5H, m), 6·54 (2H, d), 7·96~9·19 (4H, m); (Found: C, 71·61; H, 6·99; Cl, 21·38, $C_{10}H_{11}Cl$ requires C, 71·62; H, 7·11; Cl, 21·17%).

trans-2-*Phenylcyclopropylcarbinyl cyanide.* It was difficult to obtain the title compound in moderate yield from the corresponding chloride under conditions such as heating under reflux in aqueous alcohol or acetone. This substitution reaction was very sensitive to the purity of employed reagents, reaction temp and the nature of employed solvents. The presence of even a small amount of water or the employment of protic solvents may make the character of this reaction more SN-1 like, so that the cyclopropane ring may be readily cleaved. Among many attempts, the desired nitrile could be obtained in the highest yield (Y = 76·7%) according to a following procedure. *trans*-2-Phenylcyclopropylcarbinyl chloride (65 g; moles) was added dropwise to 400 ml of the anhyd dimethylformamide, freshly distilled, containing KCN (44·0 g; 0·68 moles) at 120°~130° with vigorous stirring, and after the addition, the mixture was stirred at 120°~130° for 20 h. After filtration of K-salts and removal of dimethylformamide at reduced pressure, fractional distillation of the dark-brown residue gave 41·0 g (76·7% yield) of almost pure *trans*-2-phenylcyclopropylcarbinyl cyanide, b.p. 146°~147°/14 mm; NMR ($CCl_4$): $\tau$ = 2·95 (5H, m), 7·55 (2H, d), 7·96~9·18 (4H, m); IR (neat): 2250 (—C≡N), 3070, 1025 $cm^{-1}$ (cyclopropane); (Found: C, 84·06; H, 7·13; N, 8·81. $C_{11}H_{11}N$ requires: C, 84·04; H, 7·05; N, 8·91%).

trans-2-*Phenylcyclopropylacetic acid*, trans-2-*phenylcyclopropylacetyl chloride and t-butyl per* (trans-2-*phenylcyclopropyl*) *acetate* were prepared, respectively, from the corresponding precursor according to the procedure described for the preparation of nonsubstituted derivatives. Their spectroscopic and analytical results are summarized in Table 4.

*Synthesis of t-butyl per* (trans-2-*methylcyclopropyl*) *acetate* (4) (The title peracaetate 4 was prepared according to a following reaction route.)

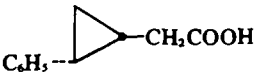
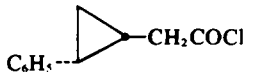
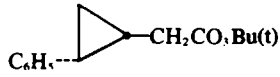
*Ethyl* (trans-2-*methylcyclopropyl*) *acetate.* Zn–Cu couple[18] (29·5 g; containing 0·46 atoms of Zn) was suspended in 160 ml anhyd ether. A crystal of $I_2$ was added and the mixture was stirred for 0·5 h. A mixture of *trans*-ethyl 2-penlenoate (41 g; 0·41 moles) (prepared from acid-catalyzed esterification of 2-pentenoic acid) and MeI (120 g; 0·45 moles) was added to the soln, and immediately a mild exothemic reaction took place. After stirring and heating under reflux for 30 h, the ether soln was decanted and the finely divided Cu and unreacted couple were washed with two 30 ml portions of ether. The combined ethereal solon was shaken with sat $NH_4Cl$ aq, $NaHCO_3$ aq and sat NaCl aq, and dried over $MgSO_4$. After removal of the drying agent and evaporation of the solvent under ordinary pressure, the residual organic components were distilled through a 30-cm column packed with Helipak. Approximately 43 g (68·5%) of ethyl (*trans*-2-methylcyclopropyl) acetate was obtained. b.p. NMR ($CCl_4$); $\tau$ = 5·90 (2H, q), 7·86 (2H, d), 8·74 (3H, t), 8·29 (3H, d), 9·10~9·98 (4H, m); (Found: C, 67·80; H, 9·85. $C_8H_{14}O_2$ requires: C, 67·57; H, 9·93%).

trans-2-*Methylcyclopropylacetic acid* was obtained from alkali hydrolysis of the corresponding ethyl ester in 69·6% yield, and *trans*-2-methylcyclopropylacetyl chloride and t-butyl per (*trans*-2-methyl-cyclopropyl) acetate were prepared according to the procedure for preparation of nonsubstituted derivatives, and their spectroscopic and analytical results are summarized in Table 5.

t-Butyl perisovalerate was prepared from isovaleric chloride according to the method mentioned above; NMR ($CCl_4$): $\tau$ = 7·86 (2H, d) 8·70 (9H, s), 8·45 (1H, m), 9·86 (6H, d); IR (neat): 1790 $cm^{-1}$ (>C=O); (Found: C, 62·25; H, 10·57. $C_9H_{18}O_3$ requires: C, 62·04; H, 10·41%).

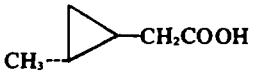
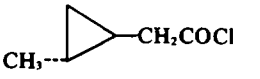
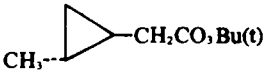
*Thermal decomposition of the peracetate* (3) *in cyclohexane.* A soln of 3 (4·96 g; 0·02 moles) dissolved in 100 ml freshly distilled anhyd cyclohexane was heated at 100° in an ampule for 24 hr. The mixture was cooled, and cyclohexane was evaporated under reduced pressure. The residue was analyzed through usual gas chromatographic technique to determine the conformation and yield of the products. (column; Silicon DC 550, 5 m; PEG 2M, 5 m). Tetralin was used as an internal standard. The analysis indicated that the product mixture consisted of **6** (Y = 6·5%), **7** (Y = 0·4%), *trans*- **8** (Y = 2·0%) **9** (Y = 9·8%), **10a** (Y = 15·1%) and three unidentified components (total yield 4·8%). (except for t-butanol, acetone and dicyclohexyl (Y = 0·8%)). All of the products were isolated through a preparative gas chromatography and identified by comparison of their gas chromatographic and

Table 4. Spectroscopic and analytical results of the derivatives of *trans*-2-phenylcyclopropyl acetic acid

| |  |  |  |
|---|---|---|---|
| Yield | 93·6% | 67·5% | 74·1% |
| b.p. (m.p.) | 109°/3 mm (45 ~ 46°C) | 105 ~ 106°/3 mm | ——— |
| IR (>C=O) | 1705 $cm^{-1}$ | 1795 $cm^{-1}$ | 1787 $cm^{-1}$ |
| NMR ($CCl_4$ ppm, τ-value) | 3·00 (m,[a] 5H)<br>7·53 (d,[b] 2H)<br>8·10 ~ 9·33 (m, 4H)<br>−1·80 (s,[c] 1H) | 2·92 (m, 5H)<br>7·12 (d, 2H)<br>8·05 ~ 9·25 (m, 4H) | 2·87 (m, 5H)<br>7·65 (d, 2H)<br>8·30 ~ 9·70 (m, 4H)<br>8·76 (s, 9H) |
| Anal. Calcd | for $C_{11}H_{12}O_2$<br>C; 74·97%, H; 6·86% | for $C_{11}H_{11}OCl$<br>C; 67·96%, H; 5·18%<br>Cl; 18·25% | for $C_{15}H_{20}O_3$<br>C; 72·55%, H; 8·12% |
| Found | C; 75·00%, H; 7·15% | C; 68·01, H; 5·21%<br>Cl; 18·32% | C; 72·67%, H; 8·16% |

[a] m = multiplet.
[b] d = doublet.
[c] s = singlet.

Table 5. Spectroscopic and analytical results of the derivatives of *trans*-2-methylcyclopropyl acetic acid

| |  |  |  |
|---|---|---|---|
| Yield | 68·5% | 58·3% | 86·5% |
| b.p. | 102°/17 mm | 48°/25 mm | ——— |
| IR (>C=O) | 1708 cm | 1795 $cm^{-1}$ | 1789 $cm^{-1}$ |
| NMR ($CCl_4$, ppm, τ-value) | 7·77 (d, 2H)<br>8·89 (d. 3H)<br>9·08 ~ 9·88 (m, 4H)<br>−1·78 (s, 1H) | 7·24 (d, 2H)<br>8·89 (d, 3H)<br>9·07 ~ 9·84 (m, 4H) | 7·76 (d, 2H)<br>8·89 (d, 3H)<br>8·75 (s, 9H)<br>8·70 ~ 9·80 (m, 4H) |
| Anal. Calcd | for $C_6H_{10}O_2$<br>C; 63·13%, H; 8·83% | for $C_6H_9OCl$<br>C; 54·35%, H; 6·84%<br>Cl; 26·74% | for $C_{10}H_{18}O_3$<br>C; 64·49%, H; 9·74% |
| Found | C; 62·94% H; 9·11% | C; 54·43%, H; 6·88%<br>Cl; 27·02% | C; 64·22%, H; 9·94% |

spectroscopic behaviour with those of the authentic samples. The following compounds which could be expected from the thermal decomposition of **3**, were synthesized according to independent reaction routes as reported, but their existence was not observed in the decomposition products; **11**, b.p. 186° ~ 187° (lit.[7] b.p. 184° ~ 186°); **12**, b.p. 160° ~ 162°/630 mm (lit.[8] b.p. 119°/152 mm); **13**, b.p. 70°/30 mm (lit.[9] b.p. 60°/15 mm).

Thermal decomposition of **3** in cyclohexene or cyclohexadiene was carried out by a similar procedure. Analytical results of the products through the gas chromatographic technique was summarized in Table 2.

*Independent preparation of the t-butyl ethers* (**8** *and* **9**). In 100 ml of anhyd THF was suspended 3·46 g (0·072 moles) of 50% solium hydride-mineral oil dispersion prewashed twice with 50 ml of anhyd ether. A soln of freshly distilled anhydrous t-butyl alcohol (5·9 g; 0·080 moles) in 20 ml anhyd THF was added slowly to the suspended soln, and then the resulting mixture was stirred under reflux for 2 h. A soln of *trans*-2-phenylcyclopropylcarbinyl chloride or phenylallylcarbinyl chloride (11 g; 0·066 moles) dissolved in 50 ml anhyd hexamethylphosphoramide was added dropwise with stirring into the cooled reaction mixture at room temp, and then the mixture was again stirred and heated under reflux for an additional 2 h. The resulting soln was poured into 500 ml water and extracted with three 100 ml portions of ether. The combined ethereal layer was dried over $MgSO_4$. After removal of the drying agent and evaporation of the solvents under reduced pressure, fractional distillation of the residual organic material gave the desired t-butyl ether.

trans-2-*Phenylcyclopropylcarbinyl t-butyl ether* (**8**); b.p. 140°/30 mm; Y = 12·3%; NMR ($CCl_4$): τ = 2·98 (5H, m), 6·69 (2H, d), 8·84 (9H, s), 8·15 ~ 9·33 (4H, m); (Found: C, 82·67; H, 10·08. $C_{14}H_{20}O$ requires; C, 82·30; H, 9·87%).

4-*Phenyl*-4-*t-butoxybutene*-1 (**9**); b.p. 138°/30 mm; Y = 10·2%; NMR ($CCl_4$): τ = 2·83 (5H, s), 3·85 ~ 4·60 (1H, m), 4·76 ~ 5·30 (2H, m), 6·62 (1H, t), 7·71 (2H, t), 8·92 (9H, s): (Found: C, 82·17; H, 10·08. $C_{14}H_{20}O$ requires; c, 82·30; H, 9·87%).

*Independent preparation of 4-substituted-4-*

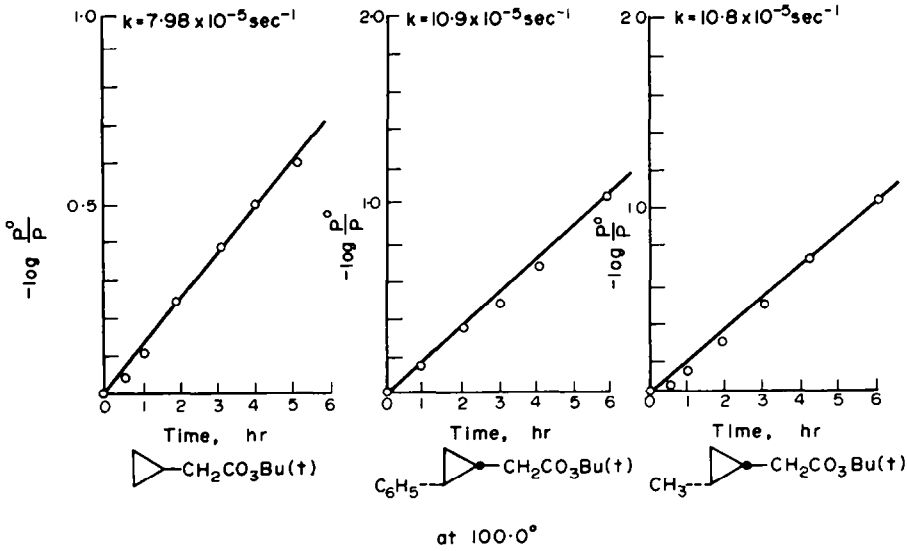



Fig 1. First order plots of thermal decomposition of the t-butyl peracetates (2–4).

*phenylbutene*-1 (**10a, b**). Into 50 ml of an ethereal soln of 0·04 moles of cyclohexyl magnesium bromide (or 3-cyclohexenyl magnesium bromide) was added dropwise moles of 4-phenyl-4-chlorobutene-1 dissolved in 50 ml of anhyd ether with stirring at room temp. Then the mixture was stirred and heated under reflux for 3 h, and was poured into 300 ml water containing ammonium chloride. The organic components were extracted with three 100 ml portions of ether and dried over $MgSO_4$. After removal of the drying agent and evaporation of the ether under reduced pressure, fractional distillation of the residue gave the desired compound in low yield.

*4-Cyclohexyl-4-phenylbutene-* (**10a**); b.p. 118°/20 mm; NMR ($CCl_4$): $\tau$ = 2·93 (5H, s), 4·12 ~ 4·87 (1H, m)m 4·95 ~ 5·40 (2H, m), 7·59 (3H, m), 8·00 ~ 9·45 (11H, m); (Found: C, 89·34; H, 10·73. $C_{16}H_{22}$ requires: C, 89·65; H, 10·35%).

*4-Cyclohexenyl-4-phenylbutene*-1 (**10b**); b.p. 120°/-22 mm; NMR ($CCl_4$): $\tau$ = 2·85 (5H, s), 4·05 ~ 4·76 (3H, m), 4·85 ~ 5·31 (2H, m), 7·54 (3H, m), 7·89 ~ 8·90 (7H, m); (Found: C, 90·3; H, 9·77. $C_{16}H_{20}$ requires: C, 90·50; H, 9·50%).

***Thermal decomposition of the t-butyl peracetate* (4) *in cyclohexane.*** Thermal decomposition of 4 in cyclohexane was carried out according to the procedure for 3. The main products consisted of n-pentane, 1,3-n-pentadiene and *trans*-2-methylcyclopylcarbinyl t-butyl ether accompanying by trace amounts of four unidentified components (except for t-butanol, acetone and dicyclohexyl). These three products were identified by spectroscopic and gas chromatographic analyses. 3-Methylbutene-1 and isoprene, expected to yield from thermal decomposition of 4, were found to be absent in the mixture through the gas chromatographic technique. trans-2-*Methylcyclopropylcarbinyl t-butyl ether* (**16**); NMR ($CCl_4$) $\tau$ = 6·89 (2H, m), 8·83 (9H, s), 8·93 (3H, d), 9·15 ~ 9·95 (4H, m); 8·83 (9H, s), 8·93 (3H, d), 9·15 ~ 9·95 (4H, m); (Found: C, 76·05; H, 12·55, $C_9H_{18}O$ requires: C, 75·99; H, 12·76%).

***Kinetic study.*** Thermal decomposition of **2 ~ 5** in cyclohexane was carried out by means of the ampule technique. Decomposition rates of these peracetates in various temps were determined by the quantitative analysis of disappearance of the peresters' carbonyl stretching bands (1780 ~ 1790 $cm^{-1}$) in their IR spectra of 1-ml aliquots. The rate constants were calculated from slopes of the least squares straight lines obtained when log P was plotted *vs* time t in following equations.[10]

$$k = \frac{2\cdot3}{t} \cdot \log \frac{Po}{P}, \qquad \frac{Po}{P} = \frac{\log T/To}{\log T/T^{\infty}}$$

To; initial concentration
Tp; concentration at time t.
$T^{\infty}$; infinitive concentration

In all cases, clean first-order kinetics were obtained up to almost quantitative completion of decomposition reactions. The rate constants at individual temperature for these peracetates shown in Table 1 were mean values of three runs, and six or seven experimental points were taken in each run. Some typical kinetic runs are illustrated in Fig 1.

## REFERENCES

[1]Part XXVIII in this series, T. Shono, K. Fujita and S. Kumai, *Tetrahedron Letters* 3393 (1973)
[2a]J. C. Martin and J. W. Timberlake, *J. Am. Chem. Soc.* **92**, 978 (1970); *Tetrahedron Letters* 4629 (1967); [b]C. Walling and P. S. Fredricks, *J. Am. Chem. Soc.* **84**, 3329 (1962); [c]H. Hart and R. A. Cipriani, *Ibid.* **84**, 3697 (1962); [d]E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.* **28**, 3442 (1963); [e]E. S. Huyser and D. T. Wang, *Ibid.* **29**, 2720 (1964); [f]C. G. Overberger and A. Lebovits, *J. Am. Chem. Soc.* **76**, 2722 (1954), etc
[3]D. C. Neckers and A. P. Schaap, *J. Org. Chem.* **32**, 22 (1967)
[4a]D. E. Appequist and J. A. Landgrebe, *J. Am. Chem. Soc.* **86**, 1543 (1964); [b]P. K. Freeman F. A. Raymond J. C. Sutton and W. R. Kindly, *J. Org. Chem.* **33**, 1448 (1968)
[5a]P. R. Schleyer and G. W. VanDine, *Ibid.* **88** 2321 (1966); [b]T. Shono, A. Oku and R. Oda, *Tetrahedron* **24**, 421

(1967); [c]T. Shono, I. Nishiguchi and R. Oda, *J. Org. Chem.* **35**, 43 (1970)
[6a]J. K. Kochi, P. J. Krusic and D. E. Eaton, *J. Am. Chem. Soc.* **91**, 1877, 1879 (1969); [b]L. M. Montgomery and J. W. Matt, *Ibid.* **89** 923, 924, 3050 (1967); [c]J. D. Roberts *et al.*, *Ibid.* **89**, 3051 (1967)
[7]P. D. Bartlett and R. R. Hiatt, *Ibid.* **80**, 1339 (1958)
[8]S. G. Beech, J. H. Turnbill and W. Wilson, *J. Chem. Soc.* 4686 (1952)
[9]R. Y. Mixer and W. G. Young, *J. Am. Chem. Soc.* **78**, 3379 (1956)
[10]E. G. E. Hawkins and R. D. Thompson, *J. Chem. Soc.* 370 (1961)
[11]P. D. Bartlett and C. Ruchardit, *J. Am. Chem. Soc.* **82** 1756 (1960)
[12]T. Shono, M. Akashi and R. Oda, *Tetrahedron Letters* 1507 (1968)
[13]W. A. Proyor, *Free Radicals.* McGraw Hill., New York, N.Y. (1966)
[14a]M. K. Kharasch J. Kuderna and W. Nudenberg, *J. Org. Chem.* **19**, 1283 (1954); [b]D. E. Detar and C. Weis, *J. Am. Chem. Soc.* **79**, 3045 (1957); [c]F. D. Greene, *Ibid.* **77**, 4869 (1955); [d]H. M. Walborsky and C. J. Chen, *Ibid.* **89** 5499 (1967)
[15]G. E. Cartier and S. C. Bunce, *Ibid.* **85**, 932 (1963)
[16]J. V. Braun, M. Kuhn and S. Siddiqui, *Ber. Dtsch. Chem. Cers* **59**, 1081 (1926)
[17]H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.* **81**, 4256 (1959)