Anal. Calcd. for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.33; H, 11.29.

2α,3α- and 2β,3β-(Difluoromethylene)-androstan-17β-ol Acetate (XIVd and XVb).—A solution of 15.0 g. (0.047 mole) of the olefin XIII in "diglyme" (500 ml.) was treated with 57.3 g. (0.376 mole) of sodium chlorodifluoroacetate as described under the above general procedure. The crude product was adsorbed from hexane on Florisil (900 g.). Elution with hexane–ether (9:1) afforded unchanged olefin XIII (3.5 g.), followed by a mixture of the adducts XIVd and XVb (10.0 g.). Fractional crystallization from methanol yielded the isomer XIVd (3.5 g.), m.p. 165–167°, [α]D +11°.

Anal. Calcd. for $C_{22}H_{32}O_2F_2$: C, 72.09; H, 8.80; F, 10.37. Found: C, 72.05; H, 8.61; F, 10.62.

From the mother liquors there was isolated the isomeric adduct XVb (1.5 g.), m.p. 130–132°, [α]D +20°.

Anal. Found: C, 72.21; H, 9.10; F, 10.54.

When the final mother liquors were rechromatographed on Florisil, there was isolated an additional quantity of unchanged olefin XIII (250 mg.) and adduct XVb (540 mg.), m.p. 130–132°. The yields of the isomeric adducts XIVd and XVd amounted to 27.5% and 16.6%, respectively.

2α,3α-(Difluoromethylene)-androstan-17β-ol (XIVe).—Saponification of the acetate XIVd (1.0 g.) was effected by leaving it overnight in 1% methanolic potassium hydroxide solution (50 ml.). The product was isolated in the usual manner and crystallized from methanol to give the alcohol XIVe, m.p. 159–160°, [α]D +19°.

Anal. Calcd. for $C_{20}H_{30}OF_2$: C, 74.06; H, 9.32; F, 11.71. Found: C, 74.07; H, 9.38; F, 11.47.

2β,3β-(Difluoromethylene)-androstan-17β-ol (XVc).—Saponification of the acetate XVb (1.5 g.) by refluxing 1 hour in 1% methanolic potassium hydroxide solution (100 ml.) furnished the alcohol XVc (1.2 g.), m.p. 146–147° after recrystallization from methanol, [α]D +15°.

Anal. Found: C, 74.42; H, 9.47; F, 12.09.

2β,3β-(Difluoromethylene)-androstan-17-one (XVd).—Oxidation of the alcohol XVc (250 mg.) in purified acetone (5 ml.) at 0° with 8 N chromic acid solution (0.25 ml.)[43] and isolation of the product in the usual manner afforded the ketone XVd, m.p. 100–102° after recrystallization from methanol, [α]D +97°.

Anal. Calcd. for $C_{20}H_{28}OF_2$: F, 11.79. Found: F, 11.57.

2α,3α-Methylene-androstan-17β-ol (XIVc) from 2α,3α-(Difluoromethylene)-androstan-17β-ol (XIVe).—A solution of the difluoro steroid XIVe (500 mg.) in ether (50 ml.) was added to a solution of sodium (600 mg.) in liquid ammonia (200 ml.) with efficient stirring. After 2 hours, ammonium chloride was added until the blue color was discharged. The product was isolated as previously described and adsorbed on Florisil (25 g.). The first two crystalline fractions obtained by elution with hexane–ether (9:1) (25 ml.) were combined (40 mg.) and crystallized from methanol to afford the cyclopropane XIVc, m.p. 128–129°, undepressed on admixture with a sample of the same derivative XIVc, similarly obtained from the 2α,3α-dichloromethylene analog XIVb, and identical with the latter by comparative infrared spectroscopy.

(43) K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); A. Bowers, T. G. Halsall, E. R. H. Jones and A. J. Lemin, *ibid.*, 2548 (1953).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Peresters. X. *tert*-Butylperoxy Chloroformate
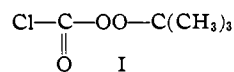
BY PAUL D. BARTLETT AND HIROSHI MINATO

tert-Butylperoxy chloroformate (I) decomposes in cumene by a concerted radical mechanism and with a half-life of 104 minutes at 60°. Its $\Delta H^{\ddagger}$ is 29.1 kcal., $\Delta S^{\ddagger}$ 10.5 cal./deg. It is an example of a perester which can decompose by the concerted mechanism with a minimum of restricted rotations. Decomposition in cyclohexene and diethyl ether is also by a radical mechanism with much chain involvement of the solvent in the latter case. The addition of lithium perchlorate to the ether medium accelerates the decomposition and converts it to an ionic mechanism of the Criegee rearrangement type. In formic acid, 60% aqueous dioxane and methanol, the decomposition of the perester appears to be entirely ionic but, whereas Criegee rearrangement predominates in formic acid, simple methanolysis occurs in methanol with very little loss of peroxidic oxygen. The aqueous dioxane medium occupies a middle position. Thus, by the choice of conditions, this one perester can be made to undergo concerted homolytic decomposition, chain decomposition involving solvent, Criegee rearrangement or simple solvolysis.

Introduction

It has been observed previously that *tert*-alkylperoxy esters of strong acids readily undergo ionic rearrangement showing strong susceptibility to acid catalysis and to media which favor ionization.[1–5] It has also been observed that when the perester can undergo homolytic fragmentation with the formation of a reasonably stable radical from the acid portion of the ester, carbon dioxide is produced quantitatively by the concerted fission of a C–C and an O–O bond.[6] This concerted decomposition, while it responds to polar substituents in the ester,[7] is not markedly dependent upon solvent.[8]

These two observations establish special interest for the perester *tert*-butylperoxy chloroformate (I) since it can be regarded as the perester of a rather strong acid and is also in a position to yield a chlorine atom by concerted decomposition. It might accordingly show enhanced tendencies toward both the ionic and the concerted radical forming types of reaction.

(1) R. Criegee, *Ann.*, **560**, 127 (1948).
(2) P. D. Bartlett and J. L. Kice, *J. Am. Chem. Soc.*, **75**, 5591 (1953).
(3) H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).
(4) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).
(5) P. D. Bartlett and T. G. Traylor, *ibid.*, **83**, 856 (1961).
(6) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).
(7) P. D. Bartlett and C. Rüchardt, *ibid.*, **82**, 1756 (1960).
(8) K. H. Lee, unpublished work in this Laboratory.

$$Cl—\overset{\displaystyle \|}{\underset{\displaystyle O}{C}}—OO—C(CH_3)_3 \qquad I$$

Preparation and Properties.—We have accordingly investigated this perester, which was first made by Davies and Hunter in 1953,[9] in some detail with respect to the rate, mechanism and products of its decomposition. When the perester is prepared by the addition of *tert*-butyl hydroperoxide to liquid phosgene at 0°, the pure material can be obtained by two distillations at 20–21° under 5 mm. pressure. The liquid perester does not explode when scratched, struck with a hammer, or heated on a spatula over a flame. Distillation at 50–60° under 120 mm. pressure occurs without violent decomposition, but the infrared spectrum of the distillate reveals some decomposition products (carbonyl bands at 5.62, 5.74 and 5.82 μ). When ten grams of the perester was allowed to stand at room temperature for an hour, it warmed spontaneously, exploded, and burned. Another specimen was successfully kept for ten hours at room temperature surrounded by a water-bath. A slightly wet sample kept at −25° for 47 days underwent slow hydrolysis developing the infrared bands of carbon dioxide and of acetone. No reaction occurred in the anhydrous perester in this period of time.

(9) A. G. Davies and K. J. Hunter, *J. Chem. Soc.*, 1808 (1953).

In aqueous acetic acid, *tert*-butylperoxy chloroformate reacted with potassium iodide liberating about 83% of the theoretical two equivalents of iodine. In thermal and hydrolytic reactions, *tert*-butylperoxy chloroformate is substantially more stable than *tert*-butyl chloroformate,[10] which decomposes at an appreciable rate at 10°.

When about 50 mg of *t*-butylperoxy chloroformate was added to 4 ml. of acrylonitrile and the mixture was degassed, the monomer polymerized to a white solid after one hour. Styrene, similarly treated, became turbid within half an hour and solidified after about four days. In each case, the degassed monomer by itself was stable.

Thermal Decomposition in Cumene.—The rate of decomposition of *tert*-butylperoxy chloroformate in cumene was measured by the loss of perester carbonyl absorption in the infrared. The kinetic plots in cumene showed good first-order behavior with only a 5% increase in rate constant with a tenfold increase in perester concentration. Accordingly, the rate constant obtained at low concentration is considered to correspond to the spontaneous thermal decomposition of the perester. The results are shown in Table I.

TABLE I

RATES OF DECOMPOSITION OF *tert*-BUTYLPEROXY CHLORO-
FORMATE IN CUMENE

Temp., °C.	Concn., mole/l.	$10^4 k_1$, sec.$^{-1}$
59.9	0.0278	1.10
	.274	1.15
70.8	.0274	4.13
	.274	4.28
80.7	.0274	15.8
	.274	15.0

The half-life of *tert*-butylperoxy chloroformate at 60° is 104 minutes, comparable to that of *tert*-butyl 4-phenyl-3-perbutenoate (II),[6] but its activation energy is quite different from the latter and is comparable rather to that of *tert*-butyl trimethylperacetate or *tert*-butyl trichloroperacetate. The activation parameters and half-lives at 60° of several peresters are compared in Table II. The fact that the rate of decomposition of

TABLE II

RATES OF DECOMPOSITION OF PERESTERS, $RCOOOC(CH_3)_3$

| R group	Half-life at 60°, min.	Activation parameters ΔH, kcal.	ΔS, cal./deg.
CH_3	500,000	38	17
Cl_3C	970	30.1	8.9
$(CH_3)_3C$	300	30.6	13
Cl	104	29.1	10.5
$C_6H_5CH{=}CHCH_2$	100	23.5	−5.9

tert-butylperoxy chloroformate is 5000 times greater than that of *tert*-butyl peracetate at 60° indicates the concerted nature of the decomposition.

$$Cl\text{---}\overset{\underset{\displaystyle O}{\|}}{C}\text{---}OO\text{---}C(CH_3)_3 \longrightarrow Cl\cdot + CO_2 + \cdot OC(CH_3)_3$$
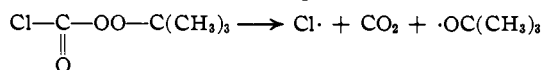
All data except those of *tert*-butylperoxy chloroformate were taken from reference 6.

The comparison between *tert*-butylperoxy chloroformate and *tert*-butyl 4-phenyl-3-perbutenoate (II) affords a particularly striking example of the relation between activation parameters and the degree of exact orientation required in the transition state. For the maximum resonance stabilization of the phenylallyl radical from the latter perester, three otherwise free rotations (at bonds marked with arrows) must be frozen

(10) A. R. Choppin and J. Rogers, *J. Am. Chem. Soc.*, **70**, 2967 (1948).

as the molecule approaches the critical point for decomposition.

II
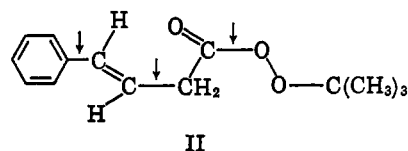
The resonance stabilization lowers the enthalpy of activation to 23.5 kcal., but the sacrifice of rotational freedom required to achieve this result lowers the entropy of activation to −5.9 cal./degree. In strong contrast is the chlorine atom which is generated from the related perester with only one rotational restriction in the molecule. Its enthalpy of activation of 29.1 kcal. and its entropy of activation of +10.5 cal./degree result in essentially the same reaction rate at 60° as for the perbutenoate.

By methods like those used in other parts of this series, the products of the decomposition in cumene were studied quantitatively, the results being given in Table III.

TABLE III

PRODUCTS OF DECOMPOSITION OF *tert*-BUTYLPEROXY CHLORO-
FORMATE IN CUMENE AT 60°

Product	Mole/mole of *tert*-butylperoxy chloroformate
Carbon dioxide	0.945
Methane	.009
Acetone	.165
tert-Butyl alcohol	.319
tert-Butyl chloride	.312
Bicumyl	.189
α,α-Dimethylbenzyl chloride	.376
Hydrogen chloride	Present
Methyl chloride	Absent
Carbonyl groups accounted for, %	94.5
tert-Butyl groups accounted for, %	79.6

The high yield of carbon dioxide is consistent with the conclusion, reached on the basis of rate studies, that the reaction occurs by the concerted breaking of two bonds. To be sure, a mechanism breaking only the O–O bond initially would also lead to a high yield of CO_2 in view of the expected instability of the chloroformate radical. However, an unconcerted mechanism could not account for the large increase in rate over that shown with *tert*-butyl peracetate. The products show a now familiar pattern with some new features superposed. Both the *tert*-butoxy radical and the chlorine atom are known to attack cumene rapidly and this is evidenced by the finding of products of the cumyl radicals in a total amount of 0.75 mole. The reaction of chlorine atoms with cumene generates hydrogen chloride whose presence was evident in the reaction product. As a result, about half of the *tert*-butyl alcohol resulting from the *tert*-butoxy radical is converted into *tert*-butyl chloride. It is normal that the decomposition of the perester in cumene should produce less acetone than *tert*-butyl alcohol, the original ratio in this case (before reaction with HCl) being apparently about 1:4. As found by other workers,[11] the amount of methane produced is very much less than that of acetone which must accompany methyl in decomposition of the *tert*-butylperoxy radical. The attack of methyl upon an aromatic solvent, with addition to the aromatic ring, takes precedence over other forms of reaction of this radical.

(11) For example, M. Levy and M. Szwarc, *ibid.*, **76**, 5981 (1954).

It was of interest to inquire whether *tert*-butylperoxy chloroformate would undergo chain decomposition in cumene similar to that observed with *tert*-butyl hypochlorite in which the chains are propagated by attack of a cumyl radical upon the chlorine of *tert*-butyl hypochlorite.[12] Although the chlorine in the present perester is rather easily removed, it is not as weakly bonded as that in a hypochlorite. The chain propagation in such a reaction would produce cumyl chloride but not bicumyl and would afford no mechanism for the formation of *tert*-butyl chloride. The presence of these other products supports the conclusion from the first-order character of the reaction that any such chain is of only minor importance.

Thermal Decomposition in Cyclohexene.—The rates of decomposition of *tert*-butylperoxy chloroformate in cyclohexene were measured by the loss of perester carbonyl absorption in the infrared. The first-order plots were linear up to about 50% of the total reaction, and a gradual retardation was noted beyond this point. The first-order rate constant was the same whether the reaction mixture was degassed or not, and was 27% higher than in cumene. The results of the rate measurements are shown in Table IV.

TABLE IV

RATES OF DECOMPOSITION OF *tert*-BUTYLPEROXY CHLORO-FORMATE IN CYCLOHEXENE AND CUMENE AT 59.9°

Run	Solvent	Degassing	Concn., mole/l.	$10^4 k_1$, sec.$^{-1}$
7	Cyclohexene	No	0.0332	1.40
8	Cyclohexene	Yes	.0365	1.36
1	Cumene	No	.0278	1.10
2	Cumene	No	.274	1.15

A study of the products obtained in cyclohexene at 60° was made and recorded in Table V.

TABLE V

PRODUCTS OF DECOMPOSITION OF *tert*-BUTYLPEROXY CHLORO-FORMATE IN CYCLOHEXENE AT 50°

Product	Mole/mole of BPCF
Carbon dioxide	0.920
Methane	.001
tert-Butyl alcohol	.781 (infrared), 0.757 (v.p.c.)
tert-Butyl chloride	.115 (v.p.c.)
Acetone	.0946 (infrared), 0.081 (v.p.c.)
2,2'-Dicyclohexenyl	.135
3-Chlorocyclohexene	.256
Carbonyl group accounted for, %	92.0
tert-Butyl group accounted for, %	99.0

The products in cyclohexene are closely analogous to those in cumene, the greater hydrogen donor power of cyclohexene being reflected in the higher ratio of (*tert*-butyl alcohol + *tert*-butyl chloride)/acetone. The 3% of the oxidation product cyclohexene-3-one is an approximate measure of the possible involvement of dissolved oxygen in the reaction. The symmetrical products in the two solvents, namely, 2,2'-dicyclohexenyl and bicumyl, are present in a ratio of 1 to 1.4 (13.5 and 18.9%), respectively) and the unsymmetrical products 3-chlorocyclohexene and α,α-dimethylbenzyl chloride are present in a ratio of 1 to 1.47. The cyclohexene, however, is poorly accounted for if indeed it possesses more reactive hydrogen than cumene. From the amount of *tert*-butyl alcohol and *tert*-butyl chloride found, there should have been 0.89 mole of cyclohexenyl radical produced during the reaction, but only 0.555 mole of this radical has been accounted for. Possibly

(12) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

disproportionation between cyclohexenyl radicals is of importance and the resulting cyclohexadiene went undetected in the solvent. 3-Chlorocyclohexene is a product of ambiguous origin since it could arise from unsymmetrical chain termination, from attack of cyclohexenyl radical on the chlorine of the original perester or from attack of cyclohexenyl radical on the O–O bond,[13,14] with subsequent decomposition of the cyclohexenyl chloroformate.

Decomposition of Diethyl Ether in the Presence and Absence of Lithium Perchlorate.—Earlier observations[15–17] have shown that diacyl peroxides and peresters become involved in chain decomposition in ether solvents, the products of the chain reaction being α-substituted ethers. It was found recently by Winstein and co-workers[18] that lithium perchlorate exerts an enormous kinetic salt effect in diethyl ether as solvent. It appeared, therefore, that this solvent would be of special interest in the study of a perester which might be capable of reaction by both radical and ionic mechanisms. The rate of decomposition of *tert*-butylperoxy chloroformate in diethyl ether was measured by the usual infrared technique. The kinetic plots in the presence of lithium perchlorate and at 35° in the absence of lithium perchlorate showed good first-order character. At 50 and 60°, undegassed samples showed a short induction period followed by a rapid increase in rate of decomposition suggesting increased chain decomposition after the oxygen in the ampoule was consumed. The results are shown in Tables VI and VII.

TABLE VI

RATES OF DECOMPOSITION OF *tert*-BUTYLPEROXY CHLOROFORMATE IN ETHER (NOT DEGASSED)

Run	Temp., °C.	Concn. of BPCF, moles/l.	Concn. of lithium perchlorate, moles/l.	$10^5 k_1$, sec.$^{-1}$
9	35.0	0.0290	...	0.260^a
10	49.5	.0290	...	^{b}
11	49.5	.0290	...	^{b}
12	59.9	.0332	...	$(23.8)^c$
13	35.0	.0278	0.100	1.57^a
14	59.9	.0290	0.103	31.5^a
15	25.8	.0290	1.10	13.7^a
16	35.0	.0290	1.10	33.7^a
17	45.0	.0290	1.10	119.0^a

^{a} Good first-order plots. ^{b} Rough; rates suddenly become larger after about 20% decomposition. ^{c} Rough.

TABLE VII

THE EFFECT OF LITHIUM PERCHLORATE ON THE RATE OF DECOMPOSITION OF *tert*-BUTYLPEROXY CHLOROFORMATE IN ETHER AT 35°

Run	Concn. of BPCF, mole/l.	Concn. of lithium perchlorate, moles/l.	Half-life, min.	Relative rate
9	0.0290	None	4420	1
13	.0290	0.100	731	6.1
16	.0290	1.100	34	129.5

When the rate constant for decomposition of the perester in cumene at 35° was calculated by extrapolation from the data of Table I, the value obtained was 0.26×10^{-5} sec.$^{-1}$, which coincides with the first-order rate constant from run 9 and indicates that this run

(13) W. von E. Doering, K. Okamoto and H. Krauch, *ibid.*, **82**, 3579 (1960).
(14) E. H. Drew and J. C. Martin, *Chem. Ind.* (London), 925 (1959).
(15) W. E. Cass, *J. Am. Chem. Soc.*, **69**, 500 (1947).
(16) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).
(17) P. D. Bartlett, E. P. Benzing and R. E. Pincock, *ibid.*, **82**, 1764 (1960).
(18) S. Winstein, S. Smith and D. Darwish, *ibid.*, **81**, 5511 (1959).

measures the spontaneous decomposition under conditions of inhibition by oxygen.

The effect of lithium perchlorate is to increase the rate of reaction greatly and to decrease the enthalpy of activation from the 29 kcal. value characteristic of cumene to 21.9 kcal. The activation parameters in ether containing 1.10 M lithium perchlorate ($\Delta H^{\ddagger}$ 21.9 kcal., $\Delta S^{\ddagger}$ −3.4 cal./deg.) are comparable with those of 9-decalyl perbenzoate[2] ($\Delta H^{\ddagger}$ 23.1 kcal., $\Delta S^{\ddagger}$ −0.9 cal./deg.), consistent with the view that the salt-induced decomposition is now entirely of the ionic type.

Table VIII shows the products obtained from decomposition of *tert*-butylperoxy chloroformate in ether at 35° without added salt and in the presence of three different concentrations of lithium perchlorate.

TABLE VIII

PRODUCTS OF DECOMPOSITION OF *tert*-BUTYLPEROXY CHLORO-FORMATE IN DIETHYL ETHER IN THE PRESENCE AND ABSENCE OF LITHIUM PERCHLORATE AT 35°

Product, moles/mole of BPCF	None	0.1 M	0.2 M	1.1 M
Carbon dioxide	0.911	(1.14)[a]	(1.00)[a]	0.841
tert-Butyl alcohol	.505	0.154	0.102	.152
tert-Butyl chloride	.255	.514	.594	.370
Ethanol	.449	.446	.316	None
Acetaldehyde	.815[b]	.286	.167	None
Methanol	None	.036	.048	0.376
Acetone	0.070	.052	.079	.273 (v.p.c.)
				.297 (infrared)
				.304 (2,4-DNP)
Acid in the liq. products	.900			.410
Chloride in the liq. products	.876			.410
tert-Butyl group accounted for	.83	0.72	0.78	.79

[a] Total condensable gas formed, probably a mixture of carbon dioxide and ether. Determination of amount of carbon dioxide was not done due to an accident. [b] The formation of 2,4-dinitrophenylhydrazone corresponded to 0.937 mole of acetaldehyde per mole of perester, assuming all the 2,4-dinitrophenylhydrazone formed is that of acetaldehyde.

The experience with the decompositions of benzoyl peroxide in ethers[16] and with di-*tert*-butyl diperoxyoxalate in isopropyl ether[17] has indicated very long kinetic chains due to reaction of the ether with the free radicals. In the present kinetic experiments, our interest was centered on comparing rates of the homolytic and heterolytic spontaneous processes and, therefore, the kinetic experiments in ether were run without degassing in the expectation that the oxygen present in solution would effectively inhibit the chain process. The rate constants shown in Table VII bear this out in general including the first-order kinetics observed throughout the run at 35° and the apperance of accleration at the higher temperatures presumably after exhaustion of the dissolved oxygen. In the product studies, on the other hand, degassing was carried out routinely. The conditions of the experiments in Table VIII are, therefore, not the same as those of Tables VI and VII and the rate of reaction in the presence of lithium perchlorate does not exceed that in its absence by the same factors as indicated in Table VII. In connection with the poor material balances in the solutions with higher salt concentration, it should be noted that with increasing concentration of lithium perchlorate there were increasing amounts of tar produced. No characterization of the chemical nature of this tar was accomplished, but it might be a polymerization product of some vinyl ethers resulting from the α-substituted diethyl ether formed in the same reaction and existing in a strongly ionizing environment. An examination of the columns in Table VIII shows a rather sudden disappearance of ethanol and acetaldehyde from the product when the lithium perchlorate concentration reaches 1.1 M compared with the pre-

vious entries in the table. Since this run also contained the largest amount of tar, it is possible that the induced free radical decomposition has not ceased to be important in this medium but that the product of it is now being converted into tarry material by a series of reactions which begins with an ionic elimination.

The only estimate that we have of the rate of decomposition of *tert*-butylperoxy chloroformate in completely degassed diethyl ether can be obtained by assigning the *tert*-butyl alcohol and chloride in the degassed product run with 1.1 M lithium perchlorate to induced radical decomposition. If we assume that the induced radical decomposition and the ionic decomposition are in the ratio 52:38 corresponding to the isolated products assigned to these two mechanisms, we conclude that the rate constant component for induced decomposition is about 1.9×10^{-4} sec.$^{-1}$ which is about 280 times the spontaneous rate in pure ether at that temperature.

Thermal Decomposition without Solvent.—Bartlett and Hiatt[6] reported that *tert*-butyl trifluoroperacetate is its own best solvent for purposes of rapid decomposition. Table IX lists the products obtained from decomposition of *tert*-butylperoxy chloroformate without solvent at 35°.

TABLE IX

PRODUCTS OF DECOMPOSITION OF *tert*-BUTYLPEROXY CHLORO-FORMATE WITHOUT SOLVENT AT 35°

Product	Mole/mole of BPCF
Carbon dioxide	0.902
tert-Butyl alcohol	.093
tert-Butyl chloride	.347
Acetone	.162
Chloroacetone	.099
Methanol	.136
Carbonyl group accounted for, %	90.2
t-Butyl group accounted for, %	70.6

Here, if we take the sum of *t*-butyl alcohol and *t*-butyl chloride as a measure of the free radical decomposition and the amount of methanol as a measure of the ionic decomposition, we conclude that at least 44% of the decomposition is homolytic and at least 14% is ionic.

Decomposition in Some Other Ionizing Solvents. Formic Acid.—The decomposition of *tert*-butylperoxy chloroformate in anhydrous formic acid is rather rapid. A conductometric measurement yielded the rate constant 1.79×10^{-3} sec.$^{-1}$ with a perester concentration of 0.005 M at 24.6°. An iodometric titration of a reaction product in formic acid by the method of Messinger[19] showed 1.02 moles of acetone produced per mole of perester. The formation of iodoform in this titration was verified by its isolation in 65% yield, m.p. 119–119.5°. These figures are consistent with an entirely ionic mechanism in formic acid leading to methyl α-chloroisopropyl ether or 2-methoxy-2-propyl chloroformate. Both these compounds are so unstable to solvolysis that they would probably be instantly attacked by formic acid and surely by water, of which only 0.009% in the medium would be required. In either case the formation of these compounds would be tantamount to the generation of hydrogen chloride, together with acetone, methanol and, in the case of the methoxychloroformate, carbon dioxide.

Thionyl Chloride.—*tert*-Butylperoxy chloroformate reacted in thionyl chloride at 23° with an approximate rate constant of 2.6×10^{-6} sec.$^{-1}$. Decrease of the perester band in the infrared was accompanied by only a small peak appearing at 5.82 μ.

(19) J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer and A. Weissberger, "Organic Analysis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1953.

TABLE X

RATES OF DECOMPOSITION OF *tert*-BUTYLPEROXY CHLORO-
FORMATE[a] IN AQUEOUS DIOXANE AT 24.6°

Run	Water, vol. %	Water, moles/l.	$10^2 k_1$, sec.$^{-1}$
18c	40	22.2	1.52
19c	26.3	14.8	1.32
20c	13.4	7.41	1.02

[a] Concentration of *tert*-butylperoxy chloroformate is ca. 0.005 M

TABLE XI

METHANOLYSIS OF *t*-BUTYLPEROXY CHLOROFORMATE IN METHA-
NOL–CARBON TETRACHLORIDE AT 24.6°[a]

Run	Methanol, vol. %	Methanol, moles/l.	$10^3 k_1$, sec.$^{-1}$
21c	100	24.8	7.90
22c	93.3	23.2	6.55
23c	86.7	21.5	5.85
24c	66.7	16.5	3.94
25c	55.3	13.2	2.77
26c	33.3	8.27	1.48
27c	20.0	4.96	0.83

[a] Concentration of *tert*-butylperoxy chloroformate was ca. 0.005 M.

TABLE XII

SUMMARY OF THE DECOMPOSITION OF *t*-BUTYLPEROXY CHLOROFORMATE IN FORMIC ACID, 60% AQUEOUS DIOXANE AND METHANOL

Solvent	Y-value	$10^3 k_1$, sec.$^{-1}$ at 24.6°	Active oxygen found, %	Acetone found, %	Iodoform found, %	Ionic rearrangement estd., %
Formic acid	2.08	1.79	..	102 (iodine)	57[a]	100
60% aqueous dioxane	0.708	15.2	58.3	25.5 (2,4-DNP)	24.5	25
Methanol	−1.052	7.90	76.0	5.7 (2,4-DNP)		5
		6.6[b]	83.4			

[a] Some iodoform was lost by sublimation. [b] By infrared method at 24°; run 29.

Dioxane–Water Mixtures.—As shown in Table X, the conductometrically measured rate of decomposition of *t*-butylperoxy chloroformate in aqueous dioxane at 24.6° is rapid and not highly sensitive to the water concentration in the region from 13 to 40% water. After 10 half-lives, 58.3 and 59.2% of the active oxygen of the perester was still found in the products, indicating that the decomposition is a simple hydrolysis at the chloroformate group. Preparation of a 2,4-dinitrophenylhydrazone indicated that about 25% of the possible acetone had been formed in this reaction. A Messinger titration yielded the figure 24.5%. These results are consistent with about 25% of the decomposition of the perester in 40% water–60% dioxane at 24.6° being by way of ionic rearrangement of the Criegee type, the rest by a simple hydrolysis of the chloroformate.

Methanol.—*tert*-Butylperoxy chloroformate reacts in anhydrous methanol at 24° with a first-order rate constant of 6.55 × 10^{-3} sec.$^{-1}$. The infrared examination of the products shows that the decrease of the perester carbonyl band at 5.51 μ is accompanied by the appearance of two new bands at 5.57 and 5.63 μ, the former being the stronger. Although methyl chloroformate has an absorption peak at 5.63 μ, the absence of this compound during and after the decomposition of the perester was shown by gas chromatography. It is quite characteristic of organic carbonates to show two carbonyl peaks when dissolved in alcohol[20] and these results are, therefore, consistent with a simple methanolysis of the perester to yield methyl *tert*-butylperoxy carbonate. In confirmation of this, a preparation of acetone 2,4-dinitrophenylhydrazone yielded

only 5.7% of the theoretical maximum after 40 half-lives of the starting material in methanol. Two iodometric titrations of such a solvolysis product after seven half-lives showed 76 and 83% of the active oxygen of the perester still present in the product.

Table XI shows the methanolysis behavior of 0.005 M solutions of *t*-butylperoxy chloroformate in carbon tetrachloride solutions containing various percentages of methanol at 24.6°. The rate declines with declining methanol concentration in a manner consistent with the methanolysis of an acid chloride[21] or, presumably, a chloroformate, but no product studies were made to determine how much decomposition of other types occurs in the more dilute methanol solutions.

The rate constant for methanolysis of *tert*-butylperoxy chloroformate as measured here is about 48 times the reported rate for methyl chloroformate and 193 times the reported rate for isopropyl chloroformate.[22] Leimu's series shows that increasing electronegativity in the alcohol part of a chloroformate increases the rate constant for methanolysis as illustrated by the fact that β-chloroethyl chloroformate reacts six times as fast as ethyl chloroformate. Table XII summarizes comparative characteristics of the reaction in three ionizing media.

It appears that ionic rearrangement 1 predominates in formic acid, while simple reaction 3 with solvent is important in methanol. The reaction in aqueous dioxane may be of type 3 or 2

Experimental

(20) H. Minato, Thesis, Harvard, 1961, pp. 93–102. Seven organic carbonates studied all showed double peaks in methanol and single ones in carbon tetrachloride. Seven out of eight esters behaved similarly. The unique double peak of benzophenone in ethanol has been reported by R. S. Becker, *J. Mol. Spectry.*, **3**, 1 (1959).

(21) H. Boehme and W. Schuerhoff, *Ber.*, **84**, 28 (1951).
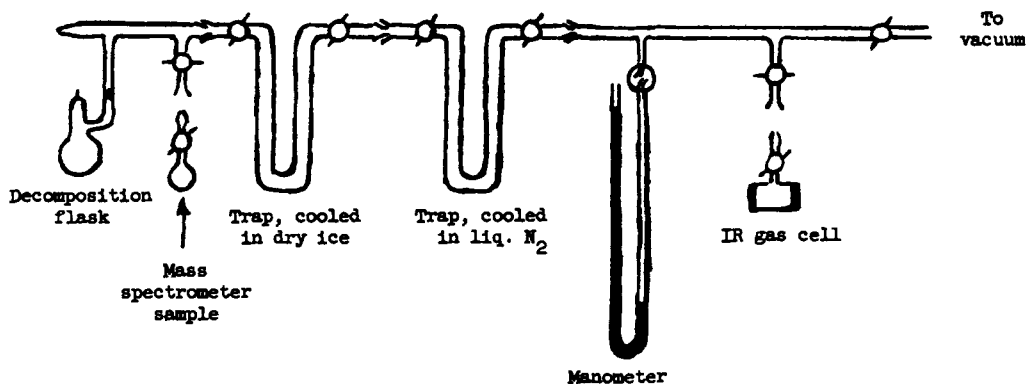(22) R. Leimu, *ibid.*, **70B**, 1040 (1937).

Fig. 1.—Vacuum system used for perester product studies.

through a 90-cm. column packed with glass helices. The center fraction boiling at 152–152.3° was stored under nitrogen atmosphere and used.

Cyclohexene.—Eastman Kodak Co. cyclohexene was distilled over sodium. The center fraction boiling at 82.5–83° was used.

Formic Acid.—Eastman Kodak Co. 98+% formic acid was refluxed with phthalic anhydride for 6 hours and then distilled.

Dioxane was purified by the method of Fieser.[23]

Diethyl Ether.—Mallinckrodt anhydrous ether was stored over sodium and used soon after a can was opened.

Lithium Perchlorate.—Reagent grade lithium perchlorate was dried in a vacuum oven at 120° for 1 day.

3-Chlorocyclohexene was prepared by boiling cyclohexene with *tert*-butyl hypochlorite and a small amount of benzoyl peroxide according to the method of Grob[24]; b.p. 76–78° (80 mm.).

α,α-**Dimethylbenzyl chloride** was prepared by the method of Klages.[25]

Chloroacetone was prepared by the method of Fritsch.[26]

tert-**Butylperoxy Chloroformate.**—*t*-Butyl hydroperoxide (12 g., 0.133 mole) was added to 20 g. of liquid phosgene (0.202 mole), and the mixture was kept at 0° for 5 hours. Then the hydrogen chloride produced and unreacted phosgene were carried away by bubbling nitrogen through the solution at room temperature, while the flask containing the mixture was kept in a water-bath. The colorless oil obtained contained a small amount of water and *tert*-butyl hydroperoxide. The oil was diluted with pentane and dried with anhydrous magnesium sulfate. Pentane was distilled off at aspirator pressure, and the crude perester was distilled with a vacuum pump. When it was distilled at 50–60° (120 mm.) clean separation from *tert*-butyl hydroperoxide was accomplished, but a part of the perester decomposed and new bands appeared at 5.63, 5.74 and 5.82 μ in its infrared spectrum. When it was distilled at 20–21° (5 mm.) a very small amount of *tert*-butyl hydroperoxide came off together with the perester, but there was no decomposition. Redistillation under the same conditions gave pure perester; yield 15.9 g. (78%). The infrared spectrum of the perester had its carbonyl band at 5.51 μ, which is one of the lowest wave lengths among the peresters known. The bands of the *tert*-butyl group appeared at 3.34, 7.26 and 7.34 μ.

Anal. Calcd. for C₅H₉O₃Cl: C, 39.36; H, 5.95; Cl, 23.24. Found: C, 39.77; H, 6.19; Cl, 22.72.

Kinetic Procedure. Infrared Method.—The method was essentially the same as that of reference 17. A weighed quantity of perester was transferred to a volumetric flask and dissolved in a solvent. About 10 to 15 aliquots of the solution were pipetted out into 100 × 13 mm. Pyrex test-tubes which previously had been drawn out. The tubes were sealed at atmospheric pressure, usually without degassing, and placed in a wire basket. The basket was immersed in the thermostated oil-bath and shaken to bring the samples to equilibrium temperature. After about 10 minutes, one of the tubes was withdrawn and immersed in a Dry Ice–acetone mixture. This was the zero time sample; the others were removed at suitable intervals in the same manner. The "infinity" sample was left in the bath for about 10 half-lives. The sample was stored at −25° until infrared analysis was carried out.

A Perkin–Elmer model 21 infrared spectrophotometer was used with cells of 0.4 mm. thickness. After collecting all the samples of a run they were allowed to warm to room temperature and diluted, if necessary, with pure solvent to bring the concentration within the range of about 20 to 100% transmission. After setting the spectrophotometer at maximum absorption on the carbonyl

(23) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co., Boston, Mass., 1957, p. 284.

(24) C. A. Grob, H. Kny and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

(25) A. Klages, *Ber.*, **35**, 2638 (1902).

(26) P. Fritsch, *ibid.*, **26**, 597 (1893).

peak, the scanning mechanism was disconnected and the pen was set at 0 and then 100% transmission using pure solvent in both cells. The samples were viewed in turn against pure solvent, care being taken to allow time for the pen to come to equilibrium with each sample. The percentage transmission T_t could be determined within ±0.3% in the range 20–80% where most of the samples fell.

The relative concentration at time t was calculated by the equation

$$p/P_0 = (\log T_\infty - \log T_t)/(\log T_\infty - \log T_0)$$

where T_∞ is the percentage transmission of the "infinity" sample viewed against pure solvent and T_0 is the percentage transmission of the first sample. The use of this sort of infinity value prevented the interference in the analysis by products of decomposition which absorbed weakly in the carbonyl region.

The validity of Beer's law was checked as follows. A solution of the perester which would give about 20% transmission was prepared. One-half of the solution was sealed in an ampoule and heated until the perester was completely decomposed, the other half was stored at −25° to prevent decomposition. Eleven solutions with relative perester concentrations of zero to ten were made up and viewed at the carbonyl absorption band of the perester against pure solvent by the usual method. A plot of $\log T_\infty - \log T$ vs. relative concentration was usually sufficiently straight through the range of percentage transmission used in the kinetic runs so that no correction for Beer's law deviations was needed. At higher concentrations the absorption was less than that expected by extrapolation by Beer's law from low concentration.

Plots of $\log (P/P_0)$ against time for decomposition of the peresters were usually straight lines. The first-order rate constants were calculated from the slopes of these lines. The enthalpies of activation, $\Delta H^{\ddagger}$, were obtained from the slopes of the lines given by $\ln (k/T)$ vs. $(1/T)$ for the runs at low concentration at three temperatures. The entropies of activation were calculated by substituting $\Delta H^{\ddagger}$ and a point on the line of $\ln (k/T)$ vs. $(1/T)$ into the equation

$$\ln (k/T) = \ln (k'/h) - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R$$

and solving for $\Delta S^{\ddagger}$ (k' = Boltzmann constant, h = Planck constant).

Conductometric Method.—An Industrial Instruments Inc. model RC16B1 conductivity bridge was used along with cells of cell constant approximately unity. The 15 ml. of solvent being used was equilibrated in the conductivity cell with the thermostated bath. Ten microliters of chloroformate was then added with a microsyringe and the cell shaken to mix the solution. Conductivity readings were started as soon as mixing was complete. In nearly all cases, the plot of $\log [(\text{conductivity})_\infty - (\text{conductivity})_t]$ against time was linear to at least 90% reaction. After the reaction was over, the hydrogen chloride formed was titrated with 0.113 N sodium hydroxide, and the chloroformate initially present was found to be usually 0.076–0.079 mmole, or 0.0050–0.0052 M. At these low concentrations, the conductivity of methanol and methanol–carbon tetrachloride solutions of *tert*-butylperoxy chloroformate was directly proportional to the acid concentration.

General Method of Product Studies.—The general technique used for analysis of the products of decomposition in various solvents was modeled after that of reference 17. A weighed amount of perester, usually about 1 g., was dissolved in 10 ml. of solvent and the solution degassed several times by alternately freezing and melting while under vacuum. The flask was then sealed under vacuum and immersed in a constant temperature bath until perester decomposition was complete. The flask was attached to the vacuum system shown schematically in Fig. 1. The flask was cooled in liquid nitrogen and opened by means of a break seal to the closed, evacuated system. The pressure of the noncondensable gas was read on the manometer, a sample taken for

mass spectrometric analysis, and the system again evacuated. The first trap was cooled by a Dry Ice–acetone mixture and the second by liquid nitrogen. The flask was allowed to warm to room temperature, the solvent distilled to the first trap and the gases condensable in liquid nitrogen were caught in the second trap. After closing the stopcock between the traps, the condensable gas was allowed to warm to room temperature and its pressure measured. Samples of the gas were then taken for infrared and mass spectral analysis. The carbon dioxide formed was absorbed on Ascarite and weighed. Any residual gas was analyzed by its infrared and mass spectra. From the pressure of the gases and the known volumes of the system, the number of moles formed was calculated.

The solvent caught in the Dry Ice cooled trap was viewed in the infrared against pure solvent and the spectrum was compared with spectra of authentic samples of possible products in the same solvent. The amount of *tert*-butyl alcohol and acetone formed was found by measurement of their absorption at 2.8 and 5.83 μ, respectively, and calibrating against known solutions. The quantitative analysis of any other volatile products found in the solvent was made by infrared or gas chromatographic methods.

The non-distilled residue left in the decomposition flask was chromatographed on silica gel and the fractions identified usually by their infrared spectra.

The gases obtained were analyzed using a Consolidated–Nier mass spectrometer, model 21-103C. A Reco Distillograph model D-2000 and a Perkin–Elmer vapor fractometer model 154-C were used for the gas chromatographic analyses.

Peresters. XI. Di-*tert*-butylperoxy Diphenylmalonate. α-Lactone Intermediates in Free Radical Reactions

BY PAUL D. BARTLETT AND LEON B. GORTLER

The chief decomposition product of di-*tert*-butylperoxy diphenylmalonate (I) in cumene is a polyester (II) of benzilic acid. The same polyester can be prepared by Staudinger's procedure of oxygenating diphenyl ketene, and in low yield by the thermal decomposition of *tert*-butylperoxy diphenylacetate without solvent. Mechanisms are proposed for the formation of diphenylacetolactone in all three reactions and the occurrence of this α-lactone is supported by controlled trapping experiments with methanol. The same mechanism is applied to the polyester obtained by Milas and Golubović from *tert*-butylperoxy isobutyrate (V). Rate and product studies are reported for I, *tert*-butylperoxy diphenylacetate and V, whose half-lives at 60° in cumene are 15, 37 and 10,000 minutes, respectively.

Introduction

In one of the extensions of our study of the concerted decomposition of peresters,[1] it was of interest to examine the behavior of double peresters which might, as a result of concerted or successive bond fissions, yield carbenes. It was with this in mind that di-*tert*-butylperoxy diphenylmalonate (I) was first

$$C_6H_5 \diagdown C \diagup C{-}OOC(CH_3)_3$$
$$C_6H_5 \diagup \diagdown C{-}OOC(CH_8)_3$$

I
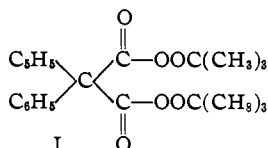
prepared. Although it soon appeared that diphenyl carbene was not formed in the course of the decomposition of this perester, other interesting and novel phenomena were observed.

Preparation and Properties of Di-*tert*-butylperoxy Diphenylmalonate.—The perester was synthesized by the dropwise addition of a solution of diphenylmalonyl chloride in ether–pentane to a cooled solution of *tert*-butyl hydroperoxide and pyridine in the same solvent. The perester, obtained in 17–25% yield, was a white crystalline solid easily recrystallized from pentane and ether. The perester melted at 66.4–67.6° with decomposition. The rate of decomposition in cumene solution was determined by following the disappearance of the perester carbonyl peak at 5.63 μ as has been done with other compounds in this series. The results yielded good first-order rate constants with no more than a 10% increase in value for a 10-fold increase in perester concentration. Table I shows the results of the kinetic studies at all three temperatures and lists the activation parameters.

A preliminary product study of the decomposition in cyclohexene gave no indication of the presence of cyclopropanes. The principal products showed absorption in the 5.6–6.1 μ region indicating the presence of car-
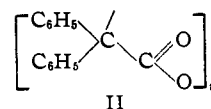
(1) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958), and later papers in this series

TABLE I

RATE CONSTANTS FOR THE DECOMPOSITION OF DI-*tert*-BUTYLPEROXY DIPHENYLMALONATE IN CUMENE

T, °C.	Concn., mole/l.	$k \times 10^4$, sec.$^{-1}$	Half-life, min.
69.8	0.175	28.8	4.0
69.8	.0175	26.3	4.4
58.9	.175	7.90	14.6
58.9	.0175	7.83	14.7
50.2	.175	2.63	43.9
50.2	.0175	2.56	45.0

$\Delta H^{\ddagger} = 25.8$ kcal./mole; $\Delta S^{\ddagger} = 4.8$ cal./deg.-mole

bonyl groups and the incomplete loss of carbon dioxide. Product studies were then carried out with cumene as solvent where it was observed that approximately 50% of the maximum amount of carbon dioxide was evolved and an amount of *tert*-butyl alcohol and acetone was found which accounted for 90% of the *tert*-butoxy groups originally present. The residue could be separated into two fractions by trituration with low-boiling petroleum ether. The insoluble fraction included the carbonyl-containing material. It did not separate into clean fractions on chromatography with silica gel or alumina. It appeared to be polymeric in character. When a benzene solution of it was evaporated, the residue was a hard lacquer which yielded a white solid on solution in ether and evaporation. The solid, which melted over a 20° range depending upon its form, evolved gas from the melt at about 200° and turned red. After refluxing for several hours with methanolic potassium hydroxide, about 20% of α-methoxydiphenylacetic acid could be obtained.

This material proved to be identical with the polyester of benzilic acid (II) prepared by Staudinger and

$$\left[\begin{array}{c} C_6H_5 \diagdown \diagup \diagdown \diagup O \\ C_6H_5 \diagup C \diagdown C \diagdown O \end{array} \right]_n$$

II

co-workers in 1925 by the oxygenation of diphenyl ketene.[2] The infrared spectrum of our product was