Conclusions

The identification of the matrix-isolated Cl^--$HCCl_2$ anion invites consideration of the hydrogen-bonded structure and models for hydrogen bonding.

The structure proposed here for the stable chloroform-electron capture product, Cl^-- - -H-CCl_2, is an unusual but straightforward intramolecular hydrogen-bonded species, which may help elucidate the bonding interaction between chloride ion and chloroform in the gas phase. Yamdagni and Kebarle[25] have studied the dissociation of the Cl^--$HCCl_3$ complex in a high-pressure mass spectrometer source and proposed a hydrogen-bonded species Cl^-- - -H-CCl_3 with a dissociation energy of 15 kcal/mol. The more recent work of Dougherty et al.[26] proposed an association ion with the structure of the S_N2 transiton state. Although the present Cl^--$HCCl_2$ species is not directly applicable to the chloride-chloroform association ion structure, the present work shows that the intramolecular hydrogen-bonded structure is relatively stable and certainly more stable than the chloroform radical anion structure.

The great intensity of ν_s and $2\nu_b$ and the reduced ν_x frequency for Cl^--$HCCl_2$ are all indicative of some charge transfer from chloride to the $HCCl_2$ radical in the hydrogen-bonded species, as has been discussed here. These observations suggest a weak covalent chloride-hydrogen chemical bonding interaction involving electron density from the chloride ion. It has been clearly shown that the halide ion-hydrogen bond strength decreases with decreasing halide ion proton affinity, which is reasonable in view of comparative sizes of the interacting species.

The inert gas matrix is an excellent medium for spectroscopic studies of hydrogen bonding, particularly when ionic systems are being investigated. The matrix provides a pseudo-gas-phase environment allowing spectroscopic data to be obtained without large solvent effects. The bands are sharp, and deuterium, carbon-13 and chlorine-37 isotopic shifts can be determined which provide information on the potential functions for the hydrogen-bonding interaction. As has been demonstrated here, the substitution of an iodide or bromide ion for chloride ion can be used to examine the spectrosopic effect of a weaker hydrogen bond in the same chemical system.

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Cyclization by Radical Displacement on Ester Groups. Conversion of Acetals to Lactones by Radical Abstraction with Stereoelectronic Control of Bond Scission

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Abstract: The thermal reactivities of monoperoxy ester monoester derivatives of diacids were examined. Kinetics and product studies of *tert*-butyl 4-carbomethoxyperbutyrate (**11**), *tert*-butyl *o*-carbomethoxyphenylperacetate (**14**), and *tert*-butyl *o*-carbobenzoxyphenylperacetate (**15**) showed that these materials react by formation of intermediate carbon centered radicals which undergo 4–9% of intramolecular radical attack on the carbonyl oxygen of the ester grouping to give lactones. The intermediate 1-alkoxy-1,4-dihydroisobenzofuran radicals **28** and **29** formed in the reactions of **14** and **15** undergo cleavage of the *O*-alkyl bond exocyclic to the ring in preference to ring opening. This was confirmed by independently generating **28** by hydrogen atom abstraction from 1-methoxy-1,4-dihydroisobenzofuran (**24**), which gave lactone **19** as the major product. A general stereoelectronic explanation is proposed to account for the direction of bond cleavage in **28** and **29**, and for other cases reported in the literature as well.

Radical displacements on carboxyl groups constitute an example of the S_H2 reaction[1] and have been most commonly observed in reactions of percarboxy groups.[2] In every case for which the position of radical attack on acylperoxy groups has been determined by isotope labeling the point of attack has been found to be peroxidic oxygen as shown in eq 1.[1,2] Thus

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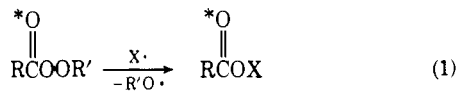
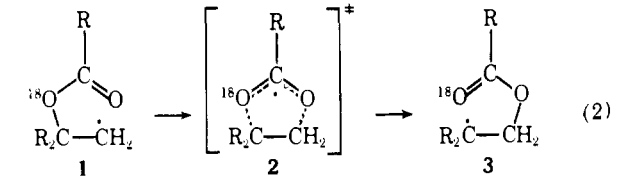


(1)

these reactions proceed through radical displacement on peroxidic oxygen.

Intramolecular radical displacements on normal ester groupings have also been reported.[3] For example β-acyloxyalkyl radicals are known to rearrange as shown in eq 2,[4] and



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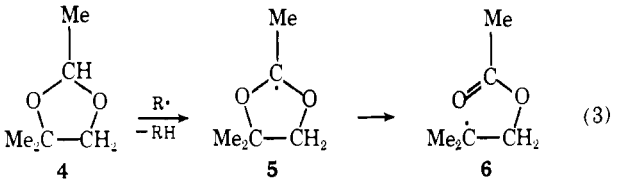
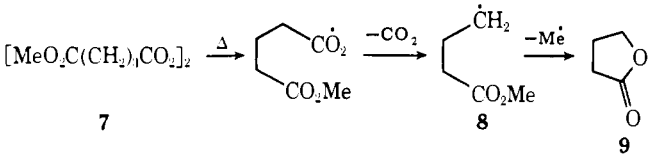


(3)

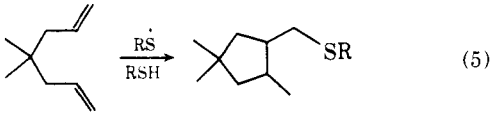
the use of ^{18}O labeling has shown that this process occurs by displacement on the carbonyl oxygen.[5a] When the dioxolanyl radical **5** was generated independently from **4** the rate of cleavage of **5** to **6** as measured by ESR was so slow as to indicate that **5** was not on the reaction coordinate between **1** and **3**, and that hence the intermediate or transition state **2** on the reaction pathway of eq 2 was not the same as **5**.[5] The structural difference between **2** and **5** demanded by this provocative hypothesis was proposed to be that, in **2**, the ring atoms and the substituent R were coplanar, whereas, in **5**, the radical center was pyramidal.[5a,c]

It has also been reported that, in the decomposition of 4-carbomethoxybutyryl peroxide (**7**), cyclization of the intermediate 3-carbomethoxypropyl radical **8** occurs to give valerolactone (**9**) to the extent of 35% (mole/mole) in acetic acid (eq 4).[6]



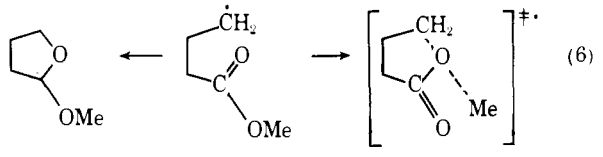
(4)

The high yield of cyclization product reported in this reaction appeared extraordinary, as such S_Hi displacements by a carbon radical on oxygen are rare.[1] Radical cyclizations involving attack on carbon–carbon double bonds as illustrated in eq 5 are well documented[7] and are of some synthetic im-



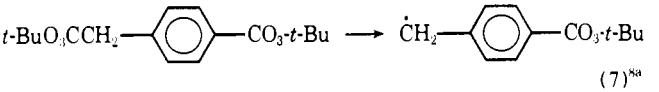
(5)

portance. Cyclizations involving displacements on peroxidic oxygens have also been observed in a number of cases.[2] It appeared however that the reaction on esters was deserving of further study to examine the scope of the reaction. The question also arose[6] as to whether the displacement involved attack on carbonyl or ethereal oxygen (eq 6).

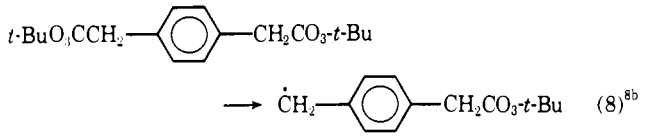


(6)

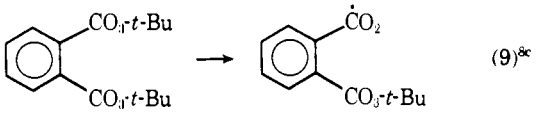
We have previously examined the reactivity of aromatic bis peresters which decompose at one perester grouping to form radical centers which have the potential of interacting with the remaining perester grouping.[8] These have included both para-substituted (eq 7, 8) and ortho-substituted systems (eq 9). It appeared therefore that study of some half-ester half-



(7)[8a]



(8)[8b]

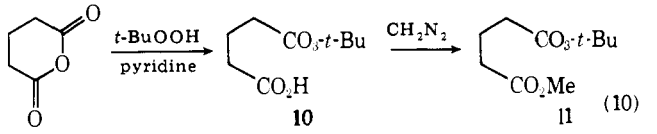


(9)[8c]

perester systems derived from appropriate dicarboxylic acids would be useful to further elucidate the reactivity of alkyl radicals in intramolecular reactions involving carboxy groups. There is also considerable interest in synthesis of lactones and their use as synthetic intermediates,[9] and exploration of free-radical cyclization routes to lactones could lead to a valuable new synthetic methodology.

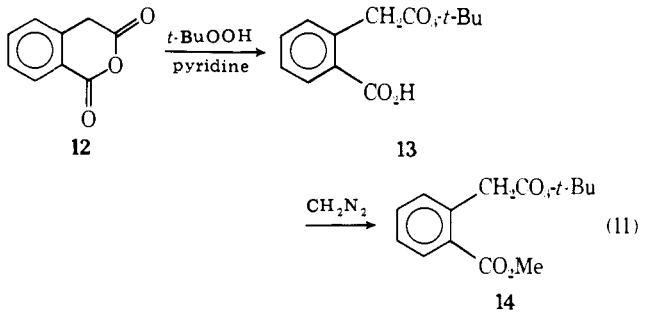
Results

Treatment of glutaric anhydride with *tert*-butyl hydroperoxide and pyridine led to *tert*-butyl 4-carboxyperbutyrate (**10**).[10a] Reaction with diazomethane gave *tert*-butyl 4-carbomethoxyperbutyrate (**11**, eq 10).[10b] The same sequence



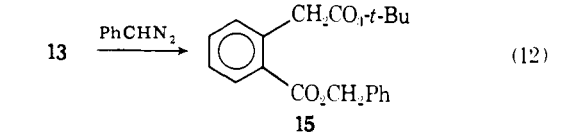
(10)

beginning with *o*-carboxyphenylacetic anhydride (**12**) gave *tert*-butyl *o*-carboxyphenylperacetate (**13**) and *tert*-butyl *o*-carbomethoxyphenylperacetate (**14**) (eq 11). When phen-



(11)

yldiazomethane[11] was reacted with **13**, *tert*-butyl *o*-carbobenzoxyphenylperacetate (**15**) was obtained (eq 12).



(12)

The kinetics of thermal decomposition of **11**, **14**, and **15** in cumene were measured and are presented in Table I together with suitable reference data for comparison. Product yields from these compounds are given in eq 13–16.

The products from the reaction of 1-methoxy-1,4-dihydroisobenzofuran (**24**) with 1 equiv of *tert*-butoxy radicals in benzene at 25 °C were also examined. Phthalide (**19**, 38%) and phthalaldehyde (**25**, 27%) were identified in the product

Table I. Kinetics of Decomposition of Peresters in Cumene

substrate	T, °C	k, s^{-1} [a]	k_{rel}	ΔH^*, kcal/mol	ΔS^*, eu
11	129.9	6.83×10^{-4}		36.1	16.1
	116.6	1.38×10^{-4}			
	99.8	1.65×10^{-5}			
	100.0[b]	1.68×10^{-5}	1.6		
$MeCO_3$-*t*-Bu[c]	100.0[b]	1.07×10^{-5}	1.00	36.9	17.2
$EtCO_3$-*t*-Bu[d]	100.0[b]	1.91×10^{-5}	1.8	33.3	8.7
14	101.0	4.38×10^{-4}		27.9	0.3
	85.4	8.07×10^{-5}	0.50		
	70.8	1.48×10^{-5}			
15	102.4	4.23×10^{-4}		30.9	7.8
	85.4	5.46×10^{-5}	0.34		
	71.0	8.84×10^{-6}			
$PhCH_2CO_3$-*t*-Bu[e]	85.4	1.61×10^{-4}	1.0	27.7	0.9

[a] Average of duplicate runs at each temperature. [b] Calculated from data at other temperatures. [c] In ethylbenzene: C. Rüchardt and I. Mayer-Ruthardt, *Chem. Ber.*, **104**, 593 (1971). [d] Reference 12. [e] Reference 8b.

$$\mathbf{11} \xrightarrow[100\ ^\circ C]{HOAc} CH_3CH_2CH_2CO_2Me\ (31\%) + t\text{-}BuO(CH_2)_3CO_2Me\ \mathbf{16}\ (17\%) + \gamma\text{-valerolactone}\ \mathbf{9}\ (6\%) \quad (13)$$

$$\mathbf{11} \xrightarrow[100\ ^\circ C]{benzene} CH_3CH_2CH_2CO_2Me\ (24\%) + t\text{-}BuO(CH_2)_3CO_2Me\ \mathbf{16}\ (26\%) + \gamma\text{-valerolactone}\ \mathbf{9}\ (4\%) + Ph(CH_2)_3CO_2Me\ \mathbf{17}\ (16\%) \quad (14)$$

$$\mathbf{14} \xrightarrow[100\ ^\circ C]{cumene} \underset{(19\%)}{\text{Me, CO}_2\text{Me}} + \underset{\mathbf{18}\ (29\%)}{\text{CH}_2\text{O-}t\text{-Bu, CO}_2\text{Me}} + \underset{\mathbf{19}\ (9\%)}{\text{lactone}} + \underset{\mathbf{20}\ (33\%)}{\text{CH}_2\text{CMe}_2\text{Ph, CO}_2\text{Me}} \quad (15)$$

$$\mathbf{15} \xrightarrow[100\ ^\circ C]{cumene} \underset{\mathbf{21}\ (25\%)}{\text{Me, CO}_2\text{CH}_2\text{Ph}} + \underset{\mathbf{22}\ (36\%)}{\text{CH}_2\text{O-}t\text{-Bu, CO}_2\text{CH}_2\text{Ph}} + \underset{\mathbf{19}\ (4\%)}{\text{lactone}} + \underset{\mathbf{23}\ (30\%)}{\text{CH}_2\text{CMe}_2\text{Ph, CO}_2\text{CH}_2\text{Ph}} \quad (16)$$

mixture (eq 17). No methyl *o*-toluate could be detected in the reaction product.

$$\underset{\mathbf{24}}{\text{OMe}} \xrightarrow{t\text{-BuO}\cdot} \underset{\mathbf{19}}{\text{lactone}} + \underset{\mathbf{25}}{\text{CHO, CHO}} \quad (17)$$

Discussion

The kinetics of the decomposition of the acyclic perester **11** are in apparent accord with rate-determining one-bond scission to give a carboxy radical which then undergoes rapid decarboxylation to radical **8** (eq 18). Thus the rate and activation parameters of **11** seem consistent with those of *tert*-butyl peracetate (Table I) for which this mechanism is generally accepted.[12,13a]

$$\underset{\mathbf{11}}{MeO_2C(CH_2)_3CO_3\text{-}t\text{-}Bu} \xrightarrow[-t\text{-BuO}\cdot]{\Delta} MeO_2C(CH_2)_3C\dot{O}_2 \xrightarrow{-CO_2} \underset{\mathbf{8}}{MeO_2CCH_2CH_2C\dot{H}_2} \quad (18)$$

The similarities in the kinetic parameters of **14** and *tert*-butyl phenylperacetate (Table I) as well as other benzylic peresters[8a,b] support rate-limiting two-bond scission leading to a benzylic radical as the preferred reaction pathway for **14** (eq 19), as is accepted for *tert*-butyl phenylperacetate.[12] The fact that the rate of **14** is lower by a factor of 2 at 85.4 °C may be ascribed to inductive electron withdrawal by the carbomethoxy group, as is commonly observed.[8a,b] The rate of **15** is very similar to that of **14** at 101 °C, and, even though the activation parameters of **14** and **15** are somewhat different, it appears certain that both react by the mechanism of eq 19.[13b]

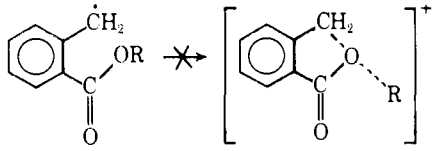
$$RCH_2CO_3\text{-}t\text{-}Bu \xrightarrow[-CO_2,\ t\text{-BuO}\cdot]{slow} R\dot{C}H_2 \quad (19)$$

The most interesting aspect of the reactivity of these peresters is the fate of the alkyl radicals generated. In the case of **8** only 4–6% of lactone was observed in either benzene or acetic acid solvent. This is somewhat less than the reported[6] formation of 18% lactone from **8** generated from the diacyl peroxide precursor (eq 4). The exact cause of this difference cannot be specified with certainty, but different amounts of cage processes would presumably give different yields of the free radical **8** from the perester and diacyl peroxide precursors.

The formation of the lactone phthalide (**19**) from either **14** or **15** shows that cyclization of the benzylic radicals **26** and **27** to lactones does indeed occur (eq 20). Further the fact that the

$$\underset{\mathbf{26}}{\text{CH}_2\cdot, \text{CO}_2\text{Me}} \xrightarrow{-Me\cdot} \underset{\mathbf{19}}{\text{lactone}} \xleftarrow{-PhC\dot{H}_2} \underset{\mathbf{27}}{\text{CH}_2\cdot, \text{CO}_2\text{CH}_2\text{Ph}} \quad (20)$$

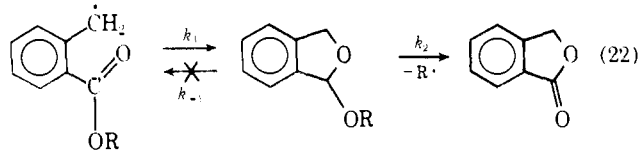
yield of **19** is approximately the same regardless of whether the source is **26** or **27** excludes a concerted displacement on the ether oxygen (eq 21) as a significant product-forming step, as



(21)

the greater stability of the benzyl radical over methyl would result in a greater yield of lactone from **27** if route 21 were followed.

The comparable yield of lactone from **26** or **27** indicates that cyclization occurs by attack on carbonyl oxygen to form the intermediates **28** and **29**, and further that this step must be essentially irreversible ($k_2 \gg k_{-1}$, eq 22). This is perhaps



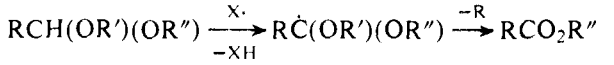
(22)

26, R = Me; **27**, R = $PhCH_2$ **28**, R = Me; **29**, R = $PhCH_2$ **19**

surprising since cleavage of **28** (R = Me) to **19** generates a methyl radical, whereas reversion to **26** forms a more stable benzylic radical.

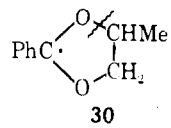
Confirmation of this result was obtained by observing the reaction of **24** with *tert*-butoxy radicals to form **19** as 38% of the volatile product (eq 17). Abstraction of hydrogen from **24** apparently can lead to **28** which then undergoes loss of a methyl radical as shown in eq 22 with high efficiency. A stereoelectronic explanation can be invoked to understand this direction of ring cleavage. As depicted in Figure 1, the orbitals of the endocyclic C–O bond are not in a position to overlap with the π system until considerable bond rotation has taken place. Furthermore, the π system formed in the transition state contains nine electrons in the delocalized π system. On the other hand cleavage of the exocyclic O–C bond permits continual overlap of the breaking bond with the π system and does not involve formation of a fully conjugated π system. The need for overlap between the p orbital of the radical and the C–O bond has been noted before.[3b]

Although the selective cleavage of **28** to give a methyl rather than a benzyl radical is unique, there is considerable precedent for the scission of dialkoxy radicals to esters. The reaction of the dioxalanyl radical **5** was cited in the introduction. The formation of dioxalanyl radicals by hydrogen atom abstraction and their subsequent ring opening was first reported by Huyser and Garcia.[14,15] Acyclic acetals also undergo hydrogen atom abstraction and subsequent cleavage of an alkyl group:[15]



(23)

In these cases the R group which is the most stable radical is preferentially lost.[16] For example benzyl cleaves 22 times faster than *n*-butyl,[16] in marked contrast to the present study. In the case of the cyclic radical **30** the bond indicated was cleavaged



30

5.3 times faster than the alternative choice,[14] but in this case there is no stereoelectronic difference between the two possible sites for cleavage. Other cases of ring opening of dioxalanyl radicals have been recently reported.[17]

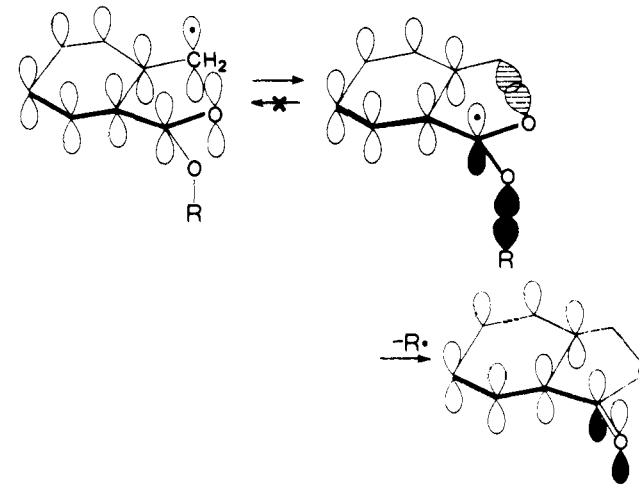
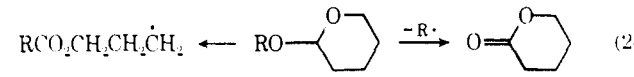


Figure 1.

Cleavage of the cyclic radicals **31** generated by abstraction of hydrogen by photoexcited benzophenone from acetals led to a strong preference for lactone formation as opposed to ring opening, leading eventually to esters via **32** (eq 24).[18] When

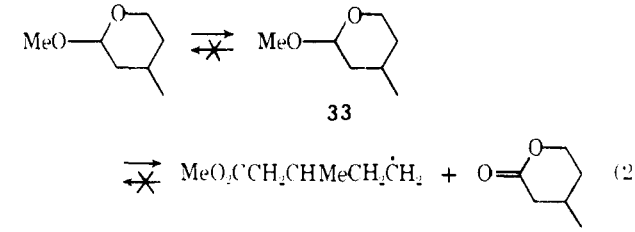


(24)

32 **31**

R was methyl the lactone/ester ratio was 16, and when R was *tert*-butyl or benzyl <1% ester was observed as opposed to lactone yields of 57–76%.

Hydrogen abstraction from the isomeric *cis*- and *trans*-2-methoxy-4-methyltetrahydropyrans also led to cyclic radicals which underwent competitive lactone and ester formation (eq 25).[19] In a typical run the ratio of lactone to ester was ~6. An



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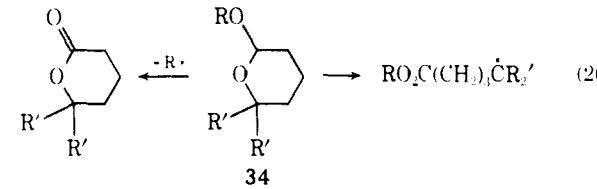
(25)

observed greater reactivity of the cis isomer was interpreted in terms of a stereoelectronic preference for abstraction of an axial hydrogen.

The reaction of the radicals **34**, also generated by hydrogen abstraction by photoexcited benzophenone, cleaved to give both lactone and ester (eq 26). When R was methyl, formation of



(26)

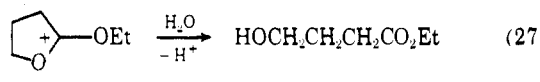
34

ester was favored for all cases where R′ was not hydrogen.

No explanation was offered[18–20] for the preference for lactone vs. ester formation observed for **31**, **33**, and **34** (R′ = H) when R is methyl. The stereoelectronic explanation that we have suggested in Figure 1 would, however, apply to these systems in that better overlap is possible between the p orbital containing the unpaired electron and the bond being broken if this is exocyclic to the ring. This rationalizes a general preference for exocyclic bond scissions that is, however, overcome in **34** when R′ is stabilizing and ring opening is favored.

In the isobenzofuranyl systems **28** and **29** the preference for exocyclic bond scission is even stronger, presumably because of the greater rigidity of the ring.

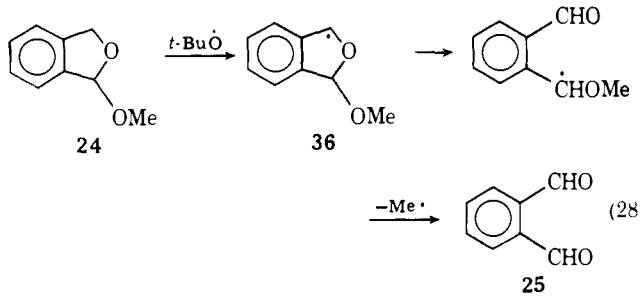
In contrast to the results with radicals, cleavage of carbonium ion **35** proceeds with a large preference for ring opening (eq 27). This direction of bond breaking permits the maximum



35 ≥95% (27)

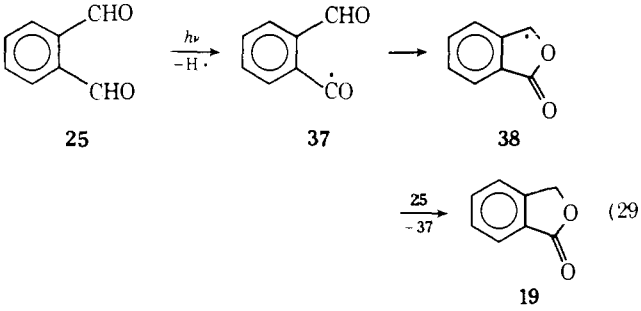
interaction of the oxygen lone pairs with the breaking bond.[21]

The formation of phthalaldehyde (**25**) from reaction of **24** with *tert*-butoxy radicals (eq 17) is also worthy of comment. A possible mechanism for this transformation is shown in eq 28. This sequence appears plausible but makes an interesting



24 **36** **25** (28)

contrast to the reported[22] photolysis of **25** at 77 K, which led to phthalide (**19**), isomeric to **25**. ESR evidence for radicals **37** and **38** was claimed[22] and **19** was proposed to arise from the sequence in eq 29. Dimers of **19** were also isolated. A variety



25 **37** **38** **19** (29)

of factors appear to affect the fate of the isobenzofuranyl radicals **28, 29, 36,** and **38.** In the case of **28** and **29** investigated here, a stereoelectronic preference leading to kinetically controlled retention of the ring system in the product is implicated. Conversion of **36** to **25** and of **38** to **19** is probably governed by irreversibility of the product-forming steps under the particular reaction conditions. The reactivities of **28** and **29** provide further examples of the expanding group of cyclic radicals in which stereoelectronic effects are significant.[23]

Experimental Section

General. Glutaric anhydride, **12, 19, 25,** and diisobutylaluminum hydride (Dibah) were obtained from Aldrich. Cumene, *tert*-butyl hydroperoxide, and pyridine were commercial materials purified as we have reported previously.[8] Elemental analyses were performed by A. B. Gygli Microanalysis, Toronto. NMR spectra were measured using a Varian T-60 instrument with Me_4Si as an internal standard. Product isolation and analysis were carried out by VPC using a Varian Aerograph Model 920 instrument. Yields of products are given as percentages of the total integrated area for all volatile products derived from the perester moiety. Gas chromatographic yields were checked by weighing fractions isolated by VPC, and the isolated yields were at least 80% of the VPC yields.

Kinetics. Rate runs were carried out by the infrared method as in our previous work[8] using a Perkin-Elmer 180 spectrophotometer. Duplicate runs at each temperature were followed to 75% reaction and showed good first-order kinetics. Rates were reproducible to ±5% and derived activation parameters are estimated to be accurate to ±1 kcal/mol in ΔH^* and ±2 eu in ΔS^*.

***tert*-Butyl *o*-carboxyphenylperacetate (13)** was obtained by adding purified *tert*-butyl hydroperoxide (3.56 g, 0.040 mol) to **12** (12.8 g, 0.079 mol) in 100 mL of a 1:1:1 ether, pentane, and CH_2Cl_2 mixture with stirring and ice cooling. Then 40 mL of pyridine in 150 mL of CH_2Cl_2 was added over a period of 1 h and the mixture was stirred overnight at ice temperature. The product mixture was then poured into cold water and extracted five times with ether and the ether extract was washed with five portions of 10% HCl and twice with water, and then dried over Drierite. During evaporation an unidentified white solid impurity crystallized which was filtered out and discarded. The filtrate was then evaporated to give a slightly yellow colored solid product which on recrystallization from $CHCl_3$–pentane gave **13** as a white solid (8 g, 0.032 mol, 80%): mp 126–128 °C; NMR ($CDCl_3$) δ 1.29 (s, 9, *t*-Bu), 4.11 (s, 2, $ArCH_2$), 7.3–8.2 (m, 4, Ar), 10.37 (s, 1, CO_2H); IR ($CDCl_3$) 1802 (C=O of perester), 1725 cm^{-1} (C=O of CO_2H).

***tert*-Butyl *o*-carbomethoxyphenylperacetate (14)** was formed by treatment of **13** with diazomethane in ether to give **14** as a yellow oil: NMR (CCl_4) δ 1.27 (s, 9, *t*-Bu), 3.80 (s, 3, CO_2Me), 3.92 (s, 2, $ArCH_2$), 7.2–7.9 (m, 4, Ar); IR (CCl_4) 1776 (C=O of perester), 1721 cm^{-1} (C=O of CO_2Me). Anal. Calcd for $C_{14}H_{18}O_5$ (mol wt, 266.29): C, 63.15; H, 6.81. Found: C, 63.56; H, 6.81.

***tert*-Butyl *o*-carbobenzoxyphenylperacetate (15)** was obtained by adding phenyldiazomethane slowly to **13** (6.0 g, 24 mmol) at 25 °C with stirring until the reaction mixture just attained a red color indicating an equivalent amount had been added. The mixture was stirred for 1 h and then poured into cold dilute HCl. The aqueous mixture was extracted five times with ether, dried with Drierite, and evaporated to give white sugar-like crystals (6.5 g, 19 mmol, 80%) which were recrystallized from pentane: mp 55–56 °C; NMR (CCl_4) δ 1.23 (s, 9, *t*-Bu), 3.97 (s, 2, $ArCH_2$), 5.27 (s, 2, OCH_2Ph), 7.3–8.0 (m, 9, Ar and Ph); IR (CCl_4) 1810 (C=O, CO_3Bu-*t*), 1747 cm^{-1} (C=O, CO_2CH_2Ph). Anal. Calcd for $C_{20}H_{22}O_5$ (mol wt, 342.39): C, 70.16; H, 6.48. Found: C, 70.88; H, 6.29.

***tert*-Butyl 4-carbomethoxyperbutyrate (11)** was obtained by slowly adding 4.5 g (50 mmol) of purified *tert*-butyl hydroperoxide and 20 mL of pyridine in 30 mL of pentane to glutaric anhydride (11.4 g, 0.10 mol) in 50 mL of 1:1 CH_2Cl_2–pentane solution at room temperature. After stirring overnight the reaction mixture was poured into 100 mL of cold water and extracted with ether. The combined organic layer was washed with dilute hydrochloric acid, NaCl solution, and water, dried over Drierite, and evaporated at room temperature to give **10**[10a] as a waxy solid (7.0 g, 34 mmol, 70%): NMR (CCl_4) δ 1.25 (s, 9, *t*-Bu), 2.2 (m, 6, $(CH_2)_3$), 9.83 (s, 1, CO_2H); IR (CCl_4) 1770 (CO_3R), 1706 cm^{-1} (CO_2H).

The methyl ester **11** was obtained by treatment of **10** with diazomethane in ether and evaporation of the ether at room temperature: NMR (CCl_4) δ 1.28 (s, 9, *t*-Bu), 2.2 (m, 6, $(CH_2)_3$), 3.60 (s, 3, CO_2Me); IR (CCl_4) 1779 (CO_3R), 1745 cm^{-1} (CO_2Me).

Products from 11 in acetic acid were determined from 1.36 g (6.2 mmol) of perester heated at 100 °C for 1 week in 5 mL of solvent in a sealed tube. The product was added to aqueous $NaHCO_3$ and extracted with ether which was then washed with dilute HCl and water and dried, and the solvent was evaporated. The product was analyzed by separation of the components by VPC using a 3 m × 12 mm 20% OV-17 on 45/60 Chromosorb W with a column temperature of 110–165 °C and He flow of 27 mL/min. Products were identified from their spectral properties as follows: methyl butyrate (31%), methyl 4-*tert*-butoxybutyrate (**16,** 17%), γ-butyrolactone (**9,** 6%), and other unidentified fractions (46%). Decomposition of **11** (1.14 g, 5.2 mmol) in benzene at 100 °C was analyzed similarly and gave methyl butyrate (24%), **16** (26%), methyl 4-phenylbutyrate (**17,** 16%), γ-butyrolactone (**9,** 4%), and unidentified material (29%). Authentic samples were available except in the case of **16** (NMR (CCl_4) δ 1.17 (s, 9, *t*-Bu), 2.1 (m, 4, $CH_2CH_2CO_2$), 3.30 (t, 2, J = 6 Hz, *t*-$BuOCH_2$), 3.60 (s, 3, CO_2Me); IR (CCl_4) 1739 cm^{-1} (C=O)) and **17** (NMR (CCl_4) δ 2.2 (m, 6, $(CH_2)_3$), 3.60 (s, 3, CO_2Me), 7.10 (s, 5, Ph); IR (CCl_4) 1748 cm^{-1} (C=O)).

Products from 14 were determined from 0.45 g (1.7 mmol) of perester heated in 5 mL of cumene for 28 h at 100 °C. The product was analyzed directly by VPC using the 20% OV-17 column to give methyl *o*-toluate (19%), methyl α-*tert*-butoxy-*o*-toluate (**18,** 29%), phthalide (**19,** 9%), and methyl α-cumyl-*o*-toluate (**20,** 33%). Products were identified by their NMR, IR, and mass spectral data. **18:** NMR

(CCl_4) δ 1.30 (s, 9, *t*-Bu), 3.85 (s, 3, CO_2Me), 4.80 (s, 2, $ArCH_2$), 7.5 (m, 4, Ar); IR (CCl_4) 1724 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* 207 (M^+ − Me, no M^+ observed). **20:** NMR (CCl_4) δ 1.27 (s, 6, Me_2), 3.38 (s, 2, $ArCH_2$), 3.75 (s, 3, CO_2Me), 7.1 (m, 9, Ar); IR (CCl_4) 1730 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* 268 (M^+). Phthalide (**19**) was identified by comparison with an authentic sample (Aldrich).

Products from 15 were determined from 0.66 g (1.9 mmol) of perester heated at 100 °C for 22 h in 5 mL of cumene in a sealed tube. Analysis as above showed phthalide (**19**, 4%), benzyl *o*-toluate (**21**, 25%), benzyl α-*tert*-butoxy-*o*-toluate (**22**, 36%), and benzyl α-cumyl-*o*-toluate (**23**, 30%). The new products were identified from their spectral data. **21:** NMR (CCl_4) δ 2.60 (s, 3, ArMe), 5.27 (s, 2, CO_2CH_2), 7.3-7.9 (m, 9, Ar); IR (CCl_4) 1724 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* 226 (M^+). **22:** NMR (CCl_4) δ 1.27 (s, 9, *t*-Bu), 4.78 (s, 2, CH_2O-*t*-Bu), 5.25 (s, 2, CO_2CH_2), 7.5 (m, 9, Ar); IR (CCl_4) 1717 cm^{-1} (C=O). **23:** NMR (CCl_4) δ 1.22 (s, 6, Me_2), 3.40 (s, 2, $ArCH_2$), 5.17 (s, 2, OCH_2), 7.30 (m, 14, Ar); IR (CCl_4) 1728 cm^{-1} (C=O). A trace of toluene (<1%) was detected in the product by the VPC retention time, including coinjection with authentic toluene.

1-Methoxy-1,4-dihydroisobenzofuran (24, 2-methoxyphthalan) was prepared by first adding diisobutylaluminum hydride (0.05 mol in toluene) in 30 min through a dropping funnel to phthalide (**19**, 6.7 g, 0.05 mol) in 100 mL of dry toluene stirred under N_2 and cooled with a dry ice-acetone bath.[24] Then 50 mL of ether was added and the solution was stirred for 4 h, the cold bath was removed, and, immediately, 150 mL more of ether was added followed by 100 mL of saturated NaCl solution. The layers were separated and the aqueous layer extracted five times with ether, the combined ether layers were dried over Drierite, and the ether was evaporated. The product was dissolved in 200 mL of MeOH and 1 mL of boron trifluoride etherate was added while the solution was cooled in ice. After 2 h of stirring, the solution was poured into saturated NaCl and extracted with pentane which was then washed with water and evaporated. Distillation gave **24** as a colorless liquid: 3.2 g (0.02 mol, 40%); bp 62-64 °C (3 mm); NMR (CCl_4) δ 3.33 (s, 3, OMe), 4.84 and 5.00 (d, 1, A portion of AB quartet of $ArCH_2$), 5.03 and 5.15 (dd, 1, B portion of AB quartet of $ArCH_2$, J = 2.5 Hz), 6.03 (d, 1, C*H*OMe, J = 2.5 Hz), 7.2 (m, 4, Ar). Anal. Calcd for $C_9H_{10}O_2$ (mol wt, 150.18): C, 71.98; H, 6.71. Found: C, 71.44, H, 6.85.

Radical abstraction from 24 was carried out with **24** (0.49 g, 3.3 mmol) and di-*tert*-butylperoxy oxalate (0.39 g, 1.65 mmol) in 5 mL of benzene at 25 °C. After 50 h the solvent was removed at water aspirator pressure and the NMR spectrum showed ~45% reaction of **24**, as judged from the decrease of the C*H*OMe peak relative to the $ArCH_2$ peak in the NMR. VPC analysis (3 m × 8 mm 30% Carbowax, 200 °C, He flow 60 mL/min) revealed phthaldehyde (**25**) and phthalide (**19**) as 27% and 38% of the volatile product, respectively. In addition a third fraction (14% of integrated area) was collected with a retention time somewhat less than that of **19** and **25**: NMR (CCl_4) δ 3.30, 5.93, 6.17, and 7.30 (each s, relative areas 6:1:1:4, respectively); mass spectrum (70 eV) *m/e* 179; no peak corresponding to methyl *o*-toluate was observed in the VPC (1% could have been detected).

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